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ON THE OPTICAL ROTATION OF PINEN HYDROCHLORIDE.

BY J. H. LONG.

Received April 28, 1899.

THE data found in the handbooks concerning the optical properties of this well-known compound, commonly called artificial camphor, are far from being in accord with each other or in accord with the actual facts. The earliest published results making pretense to accuracy are apparently those of Berthelot.[1] The conditions favoring the production of the compound from *l*-pinen or purified French turpentine oil and the physical properties of the finished substance are clearly stated. Some of the succeeding observers seem to have overlooked this earlier work and have published much less carefully controlled data.

I have elsewhere called attention to the production of this body from purified American turpentine,[2] but consider it necessary to add something to the data there presented, inasmuch as the somewhat misleading statement of Pesci[3] and Wallach, and Conrady[4] as to the inactivity of the product, have passed into the literature. See, for example, Landolt's "Optisches Drehungsvermögen," 2d ed., p. 556.

[1] *Ann. chim. phys.* [3], **40**, 5 and later.
[2] *J. Anal. Appl. Chem.*, *February, 1893.*
[3] *J. B.* (*1888*), 900.
[4] *Ann. Chem.* (Liebig), **252**, 156; *J. B.* (*1889*), 737.

The product is easily made by passing dry hydrochloric acid gas into turpentine oil, but to obtain it in pure condition it is necessary to employ a turpentine which has been purified by treatment with alkali and subsequent fractionation. The direction is usually given to cool the turpentine by immersing the container in a freezing-mixture, but this is not necessary. The maximum amount of product is not obtained at a low temperature, but at a temperature much above the freezing-point, possibly about 30° C. Inasmuch, however, as the turpentine becomes very warm during the reaction it is necessary to cool somewhat to maintain this temperature in the liquid. Marsh and Gardner[1] state that a high temperature is even better than a low temperature for production of the compound.

To determine the effect of temperature at the time of passing the gas through the turpentine the following experiment was made. Some commercial oil was allowed to stand several days over well-dried potassium carbonate, with frequent shaking, and was then poured off and treated with metallic sodium during a week in the same manner, and practically until all action ceased. The clear liquid remaining was then distilled, the higher boiling portions being rejected. From fresh American oil it is easy to obtain in this way the major portion boiling from 156° to 158°. A liter of the product so obtained which showed the specific rotation,

$$[\alpha]_D = +14.65°$$

was divided into two portions. One was poured into a flask kept cool by ice and salt, while the other was poured into a similar flask, connected with the first but allowed to stand in the air. A rapid current of dry hydrochloric acid gas was bubbled through both flasks during several hours on two days. The separation of the crystalline solid began first in the cold flask, which finally had to be disconnected to allow the gas to pass. In the second flask, which became quite warm during the reaction, 40° or above, crystallization was slow, but in the end fully as much product was obtained here as in the other. Both masses of crystals were collected on filters and allowed to drain thoroughly. They were then dissolved in hot pure alcohol and

[1] *J. Chem. Soc.*, 59, 725 (*1891*).

recrystallized by cooling. The new crystals were dissolved and crystallized again from alcohol, and the products now obtained were drained thoroughly and dried between porous plates. For polarization tests benzene solutions were made containing exactly five grams in twenty-five cc. The same specific rotation was found for the two products; *viz.*,

$$[\alpha]_D^{20} = +7.17^\circ.$$

The absolute agreement in the rotation values is probably accidental, but it is at least evident that the temperature effect cannot be important, as was indeed pointed out by Berthelot.[1] It may also be noticed that the specific rotation is about half of that of the original pinen, but this fact is without importance, as very different values are found from different oils. Some chemists give much higher values for the specific rotation. Flawitzky, for example[2], gives values between $+24^\circ$ and $+30^\circ$ for different samples. Marsh and Gardner[3] state that the specific rotation is from $+3^\circ$ to $+5^\circ$. Wallach and Conrady[4] in giving the substance as inactive state that *d*-pinen is much more readily made inactive by hydrochloric acid than is *l*-pinen, but offer no evidence to explain this view. If this were true it is likely that this effect of the acid would be heightened by increase of temperature, but observations, such as given above, show that this is not the case.

In investigations on the pinen from American oil it must be remembered that the commercial turpentine is distilled from the oleoresin from a number of distinct species of pine, and the product, as it appears in commerce, is always, and unavoidably, a mixture. The oil from any one tree undoubtedly contains both *d*- and *l*-pinen,[5] but from the long-leaf yellow pine and most other common varieties the oil obtained contains *d*-pinen in greatest abundance, while the so-called *spruce* pines of the region around Mobile, and elsewhere, yield an oil richest in *l*-pinen. As the separation of the optical antipodes by fractional distillation is

[1] *Loc. cit.*

[2] *Ber. d. chem. Ges.*, 15, 5, and Landolt's "Optisches Drehungsvermögen."

[3] *Loc. cit.*

[4] *Loc. cit.*

[5] This is not the view generally held, it being sometimes assumed that the antipodes are not present in the same plant. See Landolt's "Optisches Drehungsvermögen," Second Edition, page 116.

impossible, it will be recognized that the usual methods of obtaining dextro pinen from commercial American turpentine are entirely fallacious. It may be added here that the separation of the right and left hydrochloride by fractional crystallization appears to be equally impossible. I mixed in one trial fifty grams of a *d*-product, showing $\alpha = +1.25°$ with fifty grams of an *l*-product, showing $\alpha = -7.01°$, dissolving and crystallizing from strong alcohol in two fractions. For the first fraction I found $\alpha = -2.84°$ and for the second $\alpha = -2.85°$, while the mean calculated value of the mixture is $\alpha = -2.88°$. Practically the same result is obtained by precipitating partially by water instead of crystallizing from alcohol. These results are in accord with the observed behavior of antipodes in general, as regards solubility.

Some years ago I distilled six samples of perfectly fresh "spruce" dip, each from a single tree, and found that the oils differed in specific rotation, running from $-36.6°$ to $-40.8°$. Carefully made fractions from these oils, boiling between 156° and 156.7°, gave specific rotations between $-40.1°$ and $-42.5°$. These differences cannot be traced to oxidation or other changes due to keeping, because the liquid oleoresins distilled were fresh, were "dip" or first-year products, were sent immediately in sealed tin cans, and were distilled with steam without delay. The differences I believe to be due here and in all other cases to the presence of both *d*- and *l*-pinen in the oil of each tree. That the low rotation of many dextro oils is not due to oxidation-products is easily shown by the fact that these oils suffer but little change through treatment with alkali carbonates or the metals themselves; and further, by the fact that the old and partially dried oleoresins, known as "scrape" products, often yield oils showing as high a rotation as those from the fresh dip products.

Supposing now that the most carefully separated low-boiling fractions of American oil contain both *d*- and *l*-pinens the following experiment may suggest a reason for the low rotation of the hydrochloride from the common oil. A sample of left rotating oil treated with alkali and fractionated furnished a principal portion boiling from 156° to 157°. This showed a specific rotation:

$$[\alpha]_D^{20} = -17.11°.$$

The hydrochloride was made in the usual manner and purified by crystallization from strong alcohol. The dried fractions were dissolved in pure benzene to produce solutions containing twenty grams in 100 cc. Three fractions gave specific rotations:

1 $[\alpha]_D^{20} = -18.29°$

2 $[\alpha]_D^{20} = -18.46°$

3 $[\alpha]_D^{20} = -18.21°$

Essentially the same results were found from alcoholic solutions, and from a solution in benzene containing forty grams to 100 cc., a slightly lower value was found. While the data are insufficient to determine the true specific rotation of the pure substance it is evident that the effect of the acid was not to lessen the activity of the pinen, but to increase it. The best comparison is made by introducing the molecular rotations. For the original this is

$$[M] = -17.11° \times 136 = -2326.9,$$

and for the hydrochloride it is

$$[M] = -18.32 \times 172.5 = -3160.2,$$

from which it appears that on comparing equal molecules the rotation is much increased.

Assuming now that the action of hydrochloric acid on *l*-pinen is to increase rather than to decrease the rotating power while the action on the *d*-pinen is to produce a hydrochloride with nearly the same or probably a somewhat decreased rotation, it is apparent that from a common dextro oil the hydrochloride obtained must necessarily show a lower rotation. It could even follow that a change of sign would result, but I have not yet observed this possible case in any one of the many samples which I have converted into hydrochloride. I have found a specific rotation of less than 1° in several instances. The inactivity of the preparations from dextro American oil described by Pesci[1] and by Wallach and Conrady[2] may doubtless be accounted for in this manner. If, as Wallach assumes, the *d*-pinen becomes readily inactive under treatment with hydrochloric acid, it would

[1] *Loc. cit.*

[2] *Loc. cit.*

certainly follow that the hydrochloride from much of the dextro American oil must show a negative rotation. But this is not in agreement with the facts.

Pesci appears to be in error, with others, in giving the melting-point of the hydrochloride as 125°. A careful determination of three preparations from rather large amounts of purified and fractionated oil gives me 131° as the true melting-point, and this agrees with the value given by Riban.[1]

My thanks are due Mr. Frank Wright for valuable help in preparing samples of the hydrochloride and in determination of the optical constants.

CHICAGO, April, 1899.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 39].

SEPARATIONS OF METALLIC SULPHIDES BY MEANS OF HYDROCHLORIC ACID GAS.

BY J. BIRD MOYER.

Received April 3, 1899.

A NUMBER of quantitative separations have been made in the last few years through the agency of the haloid acids in gas form. With a few exceptions the experiments made in this laboratory and elsewhere required the use of metallic oxides or the salts of oxygen acids. The analogy of sulphur to oxygen in its derivatives led to the conclusion that similar behavior might be expected from the metallic sulphides. Smith and Keeley[1] found that arsenic sulphide, antimony sulphide, and stannic sulphide were completely volatilized in a stream of hydrochloric acid gas and that stannous sulphide, though not volatilized, was changed to stannous chloride. An attempt was made by them to effect a separation of stannic sulphide from stannous sulphide in this manner but it proved unsuccessful. Smith and Field[2] separated arsenic sulphide from vanadium sulphide quantitatively by this method.

The acid sulphides being volatile in hydrochloric acid gas it was natural to suppose that they might be separated quantitatively from the more basic metallic sulphides. It was hardly

1 Wurtz's Dictionary, Vol. V, 306 and 312.
2 This Journal, 18, 1096.
3 *Ibid.*, 18, 1051.

expected that such a course, though possible, would be pursued in ordinary analytical chemistry, yet it was thought that an investigation of this field might prove interesting. The sulphides for this purpose were precipitated, carefully washed and dried; in some cases, however, to avoid the oxidation which is common in the drying of moist sulphides, they were made by igniting the oxide in a stream of hydrogen sulphide. The dry sulphides were placed in a porcelain boat, weighed and heated in a glass combustion tube, through which was passed a current of hydrochloric acid gas.

Separation of Lead from Arsenic.—The dry sulphide of lead, not proving volatile in hydrochloric acid gas, was mixed with dry arsenic sulphide and heated until all of the arsenic was eliminated. Usually the lead sulphide changed completely to chloride and was weighed as such. It was then taken up in hot water and evaporated down with sulphuric acid and weighed as sulphate with the following results:

Expt.	PbS taken.	As_2S_3 taken.	$PbCl_2$ obtained.	$PbCl_2$ calculated.	$PbSO_4$ obtained.	$PbSO_4$ calculated.
I	0.1174	0.1045	0.1350	0.1366	....	....
II	0.3230	0.1175	0.3763	0.3758	0.4105	0.4097
III	0.1406	0.1100	0.1630	0.1636	0.1764	0.1783

In Experiment I the chloride dissolved in hot water leaving a small residue of lead sulphide, but no arsenic, which accounts for the low result.

Lead from Antimony.—The experiments with antimony did not yield results which were entirely satisfactory although this sulphide is known to be volatile. In these experiments it was found that the sulphide of antimony volatilized rapidly at first but more sluggishly toward the end, while the last traces were hard to remove. This fact makes it difficult to decide just when the separation is completed. The results obtained with antimony sulphide, prepared in the dry way, were no better. These figures were obtained:

Expt.	PbS taken.	Sb_2S_3 taken.	$PbCl_2$ obtained.	$PbCl_2$ calculated.	$PbSO_4$ obtained.	$PbSO_4$ calculated.
I	0.1837	0.2891	....	....	0.2296	0.2230
II	0.1294	0.1100	0.1513	0.1505	0.1648	0.1640

Lead from Bismuth.—Bismuth sulphide like the oxide volatilizes slowly in hydrochloric acid gas. The time required de-

pends upon the amount taken. In the first experiment the bismuth sulphide changed in the cold and volatilized at a low temperature, while in the second experiment heat was applied for three or four hours.

Expt.	PbS taken.	Bi_2S_3 taken.	$PbSO_4$ obtained.	$PbSO_4$ calculated.
I	0.1093	0.1121	0.1389	0.1386
II	0.6741	0.2638	0.8525	0.8550

There was no bismuth found with the lead after the reaction.

Cadmium from Arsenic.—Experiments with cadmium sulphide show that it does not volatilize except at a high temperature, consequently it is an easy matter to remove the arsenic from a mixture of their dry sulphides. The following results were obtained:

Expt.	CdS taken.	As_2S_3 taken.	$CdCl_2$ obtained.	$CdCl_2$ calculated.	CdO obtained.	CdO calculated.
I	0.1188	0.1143	0.1507	0.1509	....	....
II	0.1098	0.1359	....	....	0.0976	0.0959

In Experiment II, the cadmium sulphide was not all changed to chloride. The residue was, therefore, made into a paste with hydrochloric acid and pure mercuric oxide, ignited and weighed as oxide. A third experiment was tried using cadmium arsenate which was heated in hydrogen sulphide gas and then in hydrochloric acid gas.

	Gram.
$Cd_3As_2O_8$ taken	0.2497
$CdCl_2$ obtained	0.2096
$CdCl_2$ calculated	0.2109

The separation was complete in two hours at a temperature of 170° C.

Silver from Arsenic.—Silver arsenate was heated in a stream of hydrogen sulphide until it turned black. A temperature of about 190° C. was required. Hydrochloric acid gas was then substituted for the hydrogen sulphide and the temperature increased from 200° to 250°, when the mixture of silver and arsenic sulphides was visibly attacked. The mass melted, and the arsenic volatilized rapidly, leaving a white residue of silver chloride. Results:

Expt.	$Ag_3As_3O_8$ taken.	AgCl obtained.	AgCl calculated.
I	0.3292	0.3059	0.3060
II	0.5054	0.4684	0.4699

The result in Experiment I is very close to the theoretical. In the second experiment the result is good but shows a slight loss from sublimation. A higher temperature was required in the latter case to start the reaction and a naked flame was applied for a few minutes, which occasioned a faint sublimate of silver chloride just above the boat. The arsenic was found to be completely eliminated.

The above results show that it is not impossible to separate sulphides as well as oxides by means of hydrochloric acid gas. The sulphides of arsenic, antimony, and bismuth may thus be separated from lead sulphide, and the sulphide of arsenic from the sulphides of cadmium and silver. One more volatile sulphide, the sulphide of bismuth, should be included with those already mentioned. This might well be expected as the oxide volatilized in hydrochloric acid gas. This volatility of bismuth affords a method of purifying lead compounds which contain it, as its oxide or sulphide will be entirely removed by the use of hydrochloric acid gas. It is not unlikely that further separations depending upon the volatility of arsenic, antimony, tin, and bismuth sulphides may be made and the number of possible separations thus considerably increased.

The non-volatile sulphides were converted into chlorides with a variable degree of success. This in some cases depended upon the manner of their preparation. An interesting example of this was the behavior of antimony sulphide. A portion of the precipitated sulphide was heated in hydrogen sulphide to render it homogeneous, when it melted, and after cooling slowly in this gas, it crystallized nicely as stibnite. In this form it was volatilized with difficulty.

UNIVERSITY OF PENNSYLVANIA,
March 29, 1899.

THE INCANDESCENT ELECTRIC LAMP AS A SOURCE OF HEAT IN ETHER EXTRACTION.

BY C. G. HOPKINS.

Received March 20, 1899.

AS a substitute for the electric heater recently described by Sammis[1] the writer employs the ordinary incandescent lamp in extraction work. The arrangement of twenty complete

[1] This JOURNAL, 21, 42 (*1899*).

sets of Soxhlet extraction apparatus as is used in this laboratory is shown in the accompanying cut.

Five 110-volt lamps of thirty-two candle-power each are placed in the air-bath, a water-bath not being used. These are sufficient to produce a distillate amounting to about sixty drops per minute in each apparatus. The constancy of the supply of heat from the incandescent lamp is of course all that could be desired, and the fact that about ninety-six per cent. of the electrical energy is transformed into heat indicates the economy of this lamp for heating. The five lamps are connected in parallel and the current turned on or off by a single switch.

The air-bath is a galvanized iron box, thirty-six inches long, eight inches wide, and six inches deep, with double side walls and triple end walls, leaving half-inch spaces in which are placed strips of asbestos paper to decrease the loss of heat by radiation. The board upon which the bath is fastened is also covered with asbestos. The cover of the bath is removable. It contains twenty holes, arranged in two rows of ten each, which are two inches in diameter and whose centers are three and one-half inches apart each way. The lamps are placed seven inches apart, one lamp under the center of the square formed by every four holes. This symmetrical arrangement and the extra precaution taken to decrease the radiation at the ends of the bath should provide practically the same amount of heat for each set of apparatus. By actual count the rates of distillation in the twenty sets varied from twenty-nine to thirty-three drops in thirty seconds.

With the extraction in operation the temperature of the cover of the bath does not rise higher than 75°; but it has been found by experiment that, with all of the holes of the air-bath covered, it is possible to raise the temperature of the lamps to a point at which ether vapor will be ignited; so that, to be assured of *absolute* safety in case one of the flasks containing ether should break, it is necessary to employ a water-bath, the bulb of each lamp being immersed in the water.

It may be noted that the condensers are connected in sets of four, so that five streams of water (each controlled by a separate stop-cock) suffice for the twenty condensers, the water for the entire apparatus being turned on or off by a single valve.

Each condenser may be moved vertically two or three inches without interfering with the flow of water. When in use the condenser is supported by the Soxhlet apparatus; when not in use the side tube resting upon the upper board supports it. (The condensers here shown have already been described in detail.)[1]

Several hundred fat extractions have already been made with this apparatus using the electric lamp as a source of heat. It is regularly allowed to run over night and has given perfect satisfaction. Wherever a suitable electric current can be had the incandescent lamp will certainly be found preferable to the gas flame for use in ether extraction, and not only on account of its safety but also because of its greater simplicity, constancy, cleanliness, and convenience.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 9.]

CLASSIFICATIONS OF THE CARBIDES: THEIR MODES OF FORMATION, AND REACTIONS OF DECOMPOSITION.[2]

BY J. A. MATHEWS.

Received April 19, 1899.

DURING the preparation of an extended "Review and Bibliography of the Metallic Carbides,"[3] the author examined with great care the literature bearing upon the chemistry of the carbides. References dating back to 1800 were examined and continuing down to the present, the bulk of the literature being confined to a portion of the present decade. It was found that a great many gaps exist in regard to the details concerning not only the methods of formation and properties, but also concerning the composition of certain compounds which have been from time to time described as binary compounds of carbon with a metal. A great deal of the earlier work seems to be inaccurate, and recent work along this line has not confirmed the existence of some of these earlier described compounds. Enough data has been obtained to warrant the preparation of a fairly thorough classification of these inter-

[1] This Journal, **20**, 965 (*1898*).

[2] Read at the meeting of the New York Section of the American Chemical Society, April 7, 1898.

[3] Smithsonian Miscellaneous Collections, No. 1090, Washington, D. C., 1898.

esting compounds. The information obtained by reviewing all this mass of literature upon the carbides has been condensed, and is here presented in three tabular statements. The first table is a classification of all the known carbides with their formulas so far as is possible. Doubtful ones are included, but the doubt is indicated by a question mark. In the first and second columns of this table all carbides which have not been made in the electric furnace are bracketed. The classification is based (1) upon the general mode of formation, and (2) upon some distinctions in regard to their decomposition with water or hydrochloric acid. The metals entering into the carbides are classed according to their periodic relations.

Following this table the various modes of formation are classified, and the carbides which have been made by each method are grouped. The last classification is based upon typical decompositions, those reacting in the same manner toward a given reagent being grouped together.

The question marks inserted throughout these three tables suggest many interesting subjects for research and investigation. Perhaps thus calling attention to them will result in some of the uncertain points being cleared up and the gaps in our positive knowledge filled.

I. CLASSIFICATION OF THE CARBIDES.

Periodic group.	Formed in dry way by heat.		Formed in wet way.
	Decomposed by H_2O.	Not decomposed by H_2O.	
	Decomposed by fusion with caustic and by powerful oxidation. Mostly burn in halogen gases at moderate temperatures.		Decomposed by HCl. Explode at low heat.
I.	Li_2C_2, [Na_2C_2, $NaHC_2$, K_2C_2]	[Ag_2C_2, Ag_4C, Ag_2C]	$Cu_2C_2.H_2O$, $Ag_2C_2.H_2O$ $Au_2C_2.H_2O$?
II.	[MgC_2?] CaC_2, BaC_2, SrC_2, Be_4C_3 (or Be_2C)	Zn?	$HgC_2.xH_2O$
III.	Al_4C_3, YC_2, LaC_2, ThC_2	B_6C, B_2C_2	
IV.	[CeC_3] Ce_2C	CSi [C_2Si], TiC ZrC, ZrC_2 [Pb?]	
V.		VaC	
VI.	U_2C_3	Cr_3C_2, [Cr_4C], Mo_2C, W_2C	
VII.	[MnC, Mn_2C] Mn_3C		
VIII.		[$Fe_{24}C$?, Fe_8C?, Fe_4C, Fe_2C_3, Fe_2C] Fe_3C [Ni and Co?] [IrC_4?] [Pd?] [PtC_2?]	

NOTE.—Peculiar double compounds, difficult to classify, find mention in chemical literature; *e.g.*, $Al_3C_2B_{48}$, $3CbC_2.2CbN$, $Fe_7(CrMo)_8C_4$, $Fe_7(CrW)_8C_4$, $Cr_2Fe_7C_3$, Cr_3FeC_2, PtS_2C, Si_2AlC_7, Si_4C_4S, $Ti_{10}C_2N_8$.

II. REACTIONS OF FORMATION OF METALLIC CARBIDES.

1. From oxides or carbonates of metals heated with carbon in the electric furnace.

$$2LiCO_3 + 4C = Li_2C_2 + 2CO_2 + 2CO,$$
$$CaO + 3C = CaC_2 + 2CO.$$

By parallel reactions are also formed the carbides of aluminum, barium, glucinum, boron, calcium, cerium, lanthanum, lithium, manganese, molybdenum, silicon, strontium, thorium, titanium, tungsten, uranium, vanadium, yttrium, and zirconium.

2. Directly from the metals and carbon, $2K + 2C = K_2C_2$, and similarly, in the electric furnace, carbides of aluminum, boron, chromium, and iron, also at lower temperatures it has been said that carbides of silver, copper, and nickel result, also the carbides of iron in the production of iron and steel.

3. By the decomposition of certain organic compounds by heat,

(*a*) Thiocyanates of silver, bismuth, copper, iron, manganese, lead, tin, and zinc are said to decompose in this way: $Fe(SCN)_2 + \Delta = FeC + CS_2 + N_2$, provided the operation is done with exclusion of air.

(*b*) By composition of certain salts of carboxy-acids, *e.g.*,

$Ce(HCO_2)_3$ and $CeC_2O_4 + \Delta = CeC_2$?

$C_6H_4(C_3H_7)COOAg + \Delta = Ag_2C$?

$CH_3.CO.COOAg$ and $C_2H_2(COOAg)_2 + \Delta = Ag_2C_2$?

$Co_2O_3 + KHC_4H_4O_6 + \Delta =$ cobalt carbide?

(*c*) By the decomposition of hydrocarbons by heated metals,

$$\left.\begin{aligned} C_2H_2 + Na &= C_2HNa \\ C_2H_2 + 2Na &= C_2Na_2 \end{aligned}\right\} \text{so also K and Mg.}$$

$$\text{Si and Mg} + C_6H_6 \text{ vapors} + \Delta = \begin{cases} SiC_2 \\ MgC_2? \end{cases}$$

4. Acetylides: formed in wet way by passing acetylene through ammoniacal solutions of silver nitrate, cuprous chloride, and aurous thiosulphate ($Au_2S_2O_3$), or over freshly precipitated mercuric oxide.

5. The carbides of silicon, titanium, tungsten, etc., have been made from the oxides using calcium carbide as the reducing agent instead of carbon.

III. REACTIONS OF DECOMPOSITION.

1. Decomposed by water giving mostly acetylene: lithium, sodium, potassium, calcium, barium, and strontium carbides.

$$Li_2C_2 + 2H_2O = 2LiOH + C_2H_2$$
$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

2. Decomposed by hydrochloric acid, giving acetylene.

$$Ag_2C_2 + 2HCl = 2AgCl + C_2H_2.$$

So also copper, mercury and gold (?) acetylides.

3. Decomposed by water yielding methane: aluminum and glucinum carbides.

$$C_3Al_4 + 12H_2O = 3CH_4 + 2Al_2(OH)_6.$$

4. Decomposed by water giving methane and hydrogen: manganese carbide.

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$

5. Decomposed by water giving mixtures of acetylene, ethylene, methane and hydrogen: yttrium, lanthanum and thorium carbides.

6. Decomposed by water giving beside the above volatile products a residue of liquid and solid hydrocarbons; lanthanum, cerium and uranium carbides.

AN EXAMINATION OF COMMERCIAL FLOUR.[1]

BY HENRY KRAEMER.

Received April 24, 1899.

IT is now nearly two years since Professor J. U. Lloyd asked the writer to take up the microscopical examination of flour and its adulterants, especially with the view of applying a method, already proposed by the author, at the meeting of the American Pharmaceutical Association in 1894,[2] for the quantitative determination of corn-meal in flour. A careful preliminary examination of the flour and corn-meal upon the market soon indicated that a detailed study of other cereals, as well as of starch grains, was necessary before reliable and practical results could be obtained. The work upon the starch grain itself was presented, at least in part, in a paper on "The Study of Starch Grains, etc.," to the Pure Food and Drug Congress, January, 1899. It is not necessary here to dwell either upon this study or upon the results of the morphological study of the cereals, as Tschirch and Oesterle have published monographs of

[1] Presented at the joint meeting of the Cincinnati Section with the Columbus Section, University of Cincinnati, April 15, 1899.

[2] Proceedings of American Pharmaceutical Association, 1894; and *Am. J. Pharm.*, 1894.

the important anatomical features of all the prominent cereals in their "Anatomischer Atlas (Lief. 9–11). Furthermore it was found necessary to consider the various commercial varieties of wheat, the different processes of manufacture, and the by-products and their possible utilization, as well. And in this connection it may be stated that most of the information of this character is quite well known among the more intelligent and progressive millers.[1]

GENERAL EXAMINATION.

The flour examined by the author represented all grades from those selling as low as $1.50 per barrel to the very highest grades, and included the various brands known as "spring wheat," "winter wheat," "Patents," various "blends," "bakers," etc. The first step in an examination of this kind is to determine the grade of the sample under consideration. The following is the procedure then followed by the author:

1. The color test is very useful and may be employed in a dry or wet way. The latter method, however, is preferable and appears to be the one most generally employed by millers as being reliable. In the dry method the samples of flour are placed side by side on a dark-colored board, each sample occupying a space of about one by three inches and less than one-fourth inch in depth. A comparison of unknown samples with a known standard is thus readily made. In the wet method the same procedure is followed, only the board upon which the samples are arranged, is immersed in pure or distilled water at a temperature not exceeding 35° C. In the course of an hour or longer the samples develop a more or less pronounced color according to the grades represented. The author prefers the use of a colorless glass instead of the colored board, as the color effect may be varied by placing the glass upon either a dark or a light surface.

2. The "doughing test" is a very serviceable one and is employed quite extensively by brokers and commission houses. Of course the value of this test is largely dependent upon the personal element or the experience which the operator has had. In the writer's experience the following method gives results which,

[1] A very instructive article of a popular character on this subject, appeared in the March number of the *Cosmopolitan*.

though not conclusive in themselves, are fairly characteristic. On mixing from fourteen to fifteen grams of flour with ten cc. of water at the ordinary temperature, a dough is obtained which is quite cohesive and may be handled without sticking to the apparatus employed. On cool and dry days apparently less flour is required to procure a mass which is not sticky than when the temperature is warmer and the humidity greater. It was thought by the author for some time that the lower grade flours did not require as large a proportion of water to form a dough as the better grades, but the results obtained on treating numerous commercial samples in the foregoing manner would indicate that more likely the opposite is true. However this may be, the dough gives certain prominent characteristics. One of the most prominent, besides that of color, is the firmness of texture which results in some cases. In the better grade flours there results a lighter dough, which is quite elastic, whereas the lower grade flours produce a dough which is more compact.

3. The "gluten" test, which depends upon the washing out of the starch from the mass of dough, is well known to chemists. As to what gluten really is, seems not to be well established. By some writers the gluten is said to be contained in the layer of cells immediately under the pericarp or coat of the grain of wheat. Other authorities claim, however, that in this layer we find aleurone grains and oil and that the gluten is contained rather in the endosperm or reserve cells containing the starch. They ascribe to the protoplasmic threads of these cells the property of gluten. Both are nitrogenous in character and give the same reactions with Millon's reagent for such substances.

The importance of the gluten test appears to depend, according to the writer's experience, more upon its use as a qualitative than as a quantitative test. The physical characters noted above in the examination of the dough, are also found to belong to the gluten mass, obtained as stated by washing the dough with water. A microscopical examination of this glutenous mass furnishes probably the best means for determining the extent to which the flour has been refined. In the better grades of flour we find an almost transparent, delicate, fibrous mass, in which numerous starch grains are imbedded. There are, however, few or none of the hairs of the beard of the grain of

wheat and none of the fragments of the pericarp or coat of the grain. In the poorer samples of flour the hairs and fragments of the pericarp are found to increase in proportion to the decrease of the specimens in quality. From this examination it is very apparent that what is reckoned as gluten may consist of a variety of substances, besides more or less starch, as it is almost impossible to remove the last portions of the latter substance.

It is doubtful whether, as commonly reported, the baker's flours contain more gluten than the patent and other more refined flours of the modern mills. That the lower grades of flour require a greater proportion of water to form a cohesive dough is believed by the author to be due to the presence of a larger proportion of oil in these grades, the oil being contained as above stated in the so-called "gluten" layer along with the aleurone grains. Furthermore, the large quantity of gluten reported as being present in the lower grades of flour is made up, as shown above, of various foreign substances, in addition to the gluten itself.

4. The "baking" test is regarded by some manufacturers and dealers to be the most reliable of any. In determining the grade of a flour test by this the following data are taken into consideration: Weight of flour used, amount of water, yeast and salt, temperature, time required, size and weight of finished loaf, and appearance of same on cutting.

5. The "paste" test may have some significance in determining the quality of flour. The writer finds that if one gram of flour is well mixed with fifteen cc. of water and then gradually heated to boiling, with constant stirring, and allowed to boil for one minute, that the higher grades of flour give a paste which on cooling will scarcely flow at all, whereas the lower grades give a paste which is more liquid in form. In addition the paste in the former case is of a smoother consistency, the latter being characterized by a more or less granular consistency.

6. *Odor.*—Flour having a rather characteristic odor of its own, the presence of foreign substances in it has often been determined by the mere addition of boiling water to the sample. While making some experiments in heating various cereals in glycerin, a very marked odor was detected in a solution contain-

ing corn-meal. This was so pronounced and characteristic that this method was employed for determining the presence of corn-meal in flour. The *modus operandi* is as follows: One gram of flour is mixed with about ten to fifteen cc. of nearly anhydrous glycerin and heated to boiling for a few minutes. If corn-meal be present, an odor similar to that of popped corn is developed. As small an admixture as five per cent. of corn-meal may be detected in this way.

7. In addition to the more or less characteristic general tests above enumerated for determining the value of a flour, the sense of touch may likewise be utilized for this purpose. This method, however, is of value only in the hands of one whose experience has been considerable and whose sense of touch has been especially developed in this direction.

QUALITATIVE EXAMINATION.

The general examination as outlined indicates whether a flour is good, medium, or poor in quality. The more refined flours consist almost entirely of starch grains and a very delicate fibrous material. The cheaper flours contain in addition fragments of the thick-walled cells of the so-called "gluten layer," characteristic long thick-walled one-celled hairs of the beard of the wheat grain and also fragments of the pericarp or coat of the grain. In the still lower grades these tissues are present to a still greater extent.

The main object of this paper being to determine admixtures of corn-meal and flour, it may be stated that this subject must be approached with considerabe caution, as this work is based for the most part upon a comparison of the starch grains of corn and wheat. While many of the starch grains of both corn and wheat are quite characteristic, it must be stated, on the other hand, that a large proportion of them so closely resemble each other that in an admixture it is oftentimes practically impossible to distinguish the one class from the other by the methods ordinarily employed. In order to obtain conclusive results, it is necessary that a special micro-physical and micro-chemical study of these starch grains be made. It is only the micro-chemical part of this work that can be referred to at the present time. The following reagents were used for this purpose and the action of them upon the starch

grains of wheat, corn, and potato, was studied for the purpose of comparison :

1. Chloral iodine + iodine solution ; of each equal parts.
2. Chlor-zinc-iodide solution.
3. Chloral solution (saturated), water and glycerin; of each three and three-tenths parts. To this solution as much iodine is added as the solution will take up.
4. Calcium nitrate solution (thirty per cent.).
5. Chromic acid solution (fifteen per cent.).
6. Saliva.
7. Taka-diastase (saturated solution).
8. Silver nitrate solution (two per cent.).
9. Sulphuric acid (C. P. acid ninety parts, water ten parts).
10. Sodium acetate solution (fifty per cent.).
11. Potassium hydroxide solution (one-tenth per cent.).
12. Potassium nitrate solution (saturated).
13. Potassium phosphate solution (saturated).
14. Tannin solution.
15. Hydrochloric acid (five per cent.).
16. Water.

Wheat Starch.—Chloral-iodine + iodine solution (No. 1) causes the grains to become at first uniformly blue in color ; swelling of the grains soon takes place and finally alternate light blue and blue layers are observed. Chlor-zinc-iodide (No. 2) behaves similarly to the preceding reagent. Chloral and glycerin solution (No. 3) behaves similarly to No. 1, but the grain is not colored and the lacunæ or fissures are more pronounced. Calcium nitrate (No. 4) produces in fifteen minutes a strong corrosion of some of the grains, and those not acted upon by the reagent in this manner swell in one hour very perceptibly, then show a "tricheten-like"[1] development and in five hours swell enormously and finally burst. Chromic acid (No. 5) produces a similar effect upon the grains, but appears to be more pronounced in its action. Saliva (No. 6) causes in some grains the development of prominent radiations and lamellæ, in others a tricheten-like structure is developed; in five hours the grains give indications of corrosion, which in the

[1] Arthur Meyer considers the starch grain to be made up of alternate layers of two kinds of acicular crystals (which he calls "tricheten").

course of seventeen to twenty-four hours is very pronounced. Taka-diastase (No. 7) on the other hand, acts very slowly in comparison. In five hours there is little or no effect observable, the tricheten-like structure developing after this length of time and corrosion finally taking place. Silver nitrate (No. 8) has but little action upon the grains at first, in five hours the tricheten-like development appears, and later the grains swell and disintegrate. Sulphuric acid (No. 9) acts almost immediately, causes the grains to become nearly transparent and irregular in outline, and a rapid solution takes place. Sodium acetate (No. 10) causes some of the grains, in the course of five hours, to swell and others to become very much corroded. Potassium hydroxide (No. 11) produces very soon a swelling and rupture of some of the grains and in others the development of a prominent tricheten-like structure, and finally in both a slow corrosion. Potassium nitrate (No. 12) causes almost immediately a swelling and rupture of the grains, or a strong corrosion. Potassium phosphate (No. 13) produces prominent fissures with the subsequent development of rather numerous tricheten-like layers in some grains, in others there is a swelling and rupture of the grains, with finally a gradual corrosive action on both. Tannin (No. 14) produces a swelling of the grains, together with the development of rather large irregular lacunæ, and in five hours the grains become very much swollen and of irregular shape, after which disintegration and solution takes place. Hydrochloric acid (No. 15) causes the appearance of prominent tricheten in some of the grains in a few hours, in others there is a tendency to swell, and both kinds finally divide into two or more parts. Water (No. 16) at a temperature between 50° and 70° C. produces a marked effect upon the grains; those digested at a temperature between 50° and 55° C. for several hours, are swollen, and in many cases are even ruptured; at 60° C. they show a prominent tricheten-like structure, which is scarcely visible at 65° C., and after digestion at 70° C. for one hour the grains become very irregular and swollen and are apparently not further effected by a temperature between 70° and 95° C.

Corn Starch.—Chloral-iodine + iodine solution (No. 1) causes some of the grains to swell in five hours and others to show a tricheten arrangement of the layers; the grains do not appear

to be swollen to the extent that the wheat grains are, and therefore show apparently a deeper color with the iodine. Chlorzinc-iodide (No. 2) brings out immediately the fissure or point of growth, which is in marked contrast to the wheat starch; in the course of several hours the grains swell at one end, the portion showing the swelling becomes light blue, and finally almost colorless, while the other portion remains of a deep blue color; some of the grains finally disintegrate into several portions. Chloral and glycerin (No. 3) causes the appearance of lenticular, somewhat irregular, or more or less star-shaped and prominent lacunæ or fissures, and in the course of twenty-four hours in some grains prominent radiations are developed, whereas in others a marked swelling takes place. Calcium nitrate (No. 4) makes the point of growth more visible as with previous reagents, then strong radiations or a tricheten-like structure develops in some grains, whereas in other grains the fissures develop into large radiating canals, which extend to the margin of the grain, the swelling continuing so that in five hours only the outline of the grain is visible. Chromic acid (No. 5) causes a prominent swelling of the more or less star-shaped point of growth, which continues to such an extent in some cases as to produce a rupture of the grain at one of the angles; in other cases there are numerous radiations, or a tricheten-like structure, developed around the swollen fissures, which finally disappear as the grain swells and breaks down. Saliva (No. 6) acts upon the grain very much like chromic acid and calcium nitrate, only instead of a swelling of the grain we have a rather slow corrosion in the course of forty-eight hours following the pronounced development of fissures. Taka-diastase behaves like saliva, only the corrosive action is more rapid. Silver nitrate (No. 8) causes the formation of prominent and angular fissures, which become more or less circular in outline, and near the periphery prominent radiations may develop. Sulphuric acid (No. 9) produces in some of the grains marked development of an angular fissure which becomes circular or radiating in outline, whereas in others a corrosive action appears to begin at the periphery of the grain, followed by gradual solution of the entire grain. Sodium acetate (No. 10) behaves very much like calcium nitrate. Potassium hydroxide (No. 11) acts simi-

larly on the grain to calcium nitrate and sodium acetate. Potassium nitrate (No. 12) differs in its action on corn very markedly from that on wheat, in that there is a strong development of radiating fissures which extend in many cases to the periphery, whereas in wheat there is a more pronounced swelling of the grains and an irregular corrosive action. Potassium phosphate (No. 13) causes the development of a prominent lenticular, or star-shaped fissure, which increases in size and in seventeen to twenty-four hours there is a complete breaking-down of the grain. Tannin (No. 14) causes also the immediate production of prominent fissures which in five hours develop into large canals, or circular portions, and there is finally a separation of the grain into several parts. Hydrochloric acid (No. 15) causes in some cases the development of large star-shaped or lenticular fissures, and in other cases in the course of but twenty minutes there is a marked swelling of the grain at one point, which continues until disintegration takes place. Water (No. 16), between the temperature of 50° and 70° C., causes certain characteristic features to be developed; the grains when heated for one and a half hours at 50° C., develop in most cases a rather pronounced circular fissure, in other grains there may be a swelling or lenticular or star-shaped fissure; at 55°–60° C. the swelling of the grain is more pronounced, and at 65° C. the remainder of the grains show a marked one-layered tricheten-like structure; at 70° C. the markings have disappeared and the grains have become swollen to angular and irregular masses.

In comparing the results of the aforesaid experiments some general observations may be made. We find that we have at least two different kinds of starch grains in each class. The wheat starch grains are either (1) nearly spherical or elliptical in outline without any prominent point of growth, or (2) are characterized by a many-armed fissure looking like the stone cells in tea leaves. The corn-starch grains are either (1) four to six angled and possess a pronounced lenticular or star-shaped fissure, or (2) are nearly spherical with a more or less circular point of growth. Number one in each of these two classes may be said to represent the typical wheat starch and corn starch grain. The tricheten-like structure already referred to appears to be developed by the action of the reagent in less time

and at lower temperatures in wheat grains than is required to produce this effect in the corn starch. Furthermore, a marked difference in size is manifest in the starch grains of corn and wheat when mounted in water and when swollen by the various reagents. Wheat starch grains when examined in water are one to forty-two microns in diameter, the typical grain for purposes of study being about seventeen microns in diameter; when swollen the grains range in diameter from three to seventy microns, the typical being about fifty-three microns. The starch grains of corn when examined in water are from one to twenty-one microns in diameter, the typical grain being about fourteen microns in diameter; when swollen the grains range in size from four to forty-four microns, the typical being about fifty-three microns in diameter.

QUANTITATIVE EXAMINATION.

It is essential before making a quantitative microscopical examination of flour that a general and qualitative examination, as already described, be made. The author, as stated, in the preface of this paper, proposed some years ago a method for the valuation of powdered drugs and foods, by means of the microscope. This was subsequently elaborated in a paper published in 1897.[1] Inasmuch as the method used at that time is applicable to the present work some of the most important details are here given.

(1) The same *reagents* and mounting media are employed in doing quantitative work as were considered in the qualitative examination of the flour.

(2) The quantity of flour to be examined by means of the microscope must represent the sample in every particular; in other words, the *sampling must be done properly* and in accordance with the methods used in the assay of ores. While the quantity to be examined may consist of but a few grams, it must thoroughly represent the lot of flour on which value is to be given.

(3) The amount of sample used in the examination is generally about $\frac{1}{256}$ gram (= 0.0039 gram = 0.06 grain). The quantity of flour may be weighed out, or, what is more con-

[1] See Proceedings of the American Pharmaceutical Association, 1897; also American Journal of Pharmacy, October, 1897.

venient, with practice, a gram is weighed out and divided with a spatula, as follows:

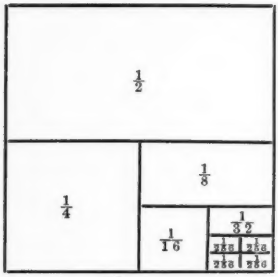

Fig. 1.

$\frac{1}{2} = 0.500$ gram.
$\frac{1}{4} = 0.250$ "
$\frac{1}{8} = 0.125$ "
$\frac{1}{16} = 0.0625$ "
$\frac{1}{32} = 0.03125$ "
$\frac{1}{128} = 0.0078$ "
$\frac{1}{256} = 0.0039$ "

(4) The cover-glasses used, whether round or square, *should be uniform in size and thickness* for comparison of the mounts of the standards with those of the specimen to be tested.

(5) The *amount of reagent* employed in making a mount must be just sufficient to float the cover-glass, and as few air-bubbles as possible are permitted to be formed.

(6) *A homogeneous mixture* of sample with reagent must be formed before the cover-glass is put down. This is best done by taking the edge of the cover-glass in a pair of forceps and distributing the powder in the mounting media or reagent.

(7) After the mount has been made and the sample examined previously qualitatively, the quantitative estimation of the powder is made. This is based on one or more of the structures or constituents that are characteristic of the sample.

When samples of lower grades of flour are examined the fragments of the pericarp, thick-walled cells of the so-called "gluten layer" and the characteristic hairs of the beard are the structures discerned. In the examination of flour containing corn-meal, the typical starch grains of the latter are selected as a basis for the determination.

The employment of the ocular micrometer, ruled in 100 square millimeters (proposed by the author in 1894), or of the ordinary ocular micrometer (proposed by the author in 1897), is not applicable in the examination of flour as the typical corn starch grains and tissues found in inferior grades of flour are not sufficiently numerous to warrant this procedure. The method best adapted for

the examination of these grades consists in the employment of either the high or low power objective and counting the number of typical starch grains or characteristic tissues which are found in examining five portions of the mount, as indicated by the diagram.

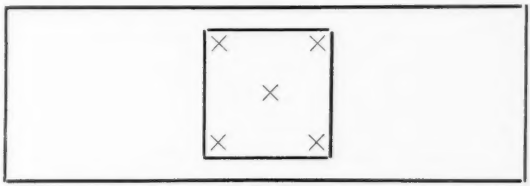

Fig. 2.

When the flour does not contain any corn-meal the low power objective is employed. When corn-meal is present the high power objective (one-fourth to one-eighth inch) is necessary.

(8) *The number of mounts* to be made of the standard and the sample under examination should generally not be less than twelve each. But as two to three mounts can be made upon the same slide, from four to six slides only are necessary for each sample.

(9) If the sample is found to be a mixture, a similar compound, representing the proportions found, should be made up, and the powder under investigation be compared with it.

It is thus apparent that the quantitative results are wholly dependent upon comparisons of an unknown with a known sample. The conditions must be nearly the same in both. The sampling must be done similarly; the same amount of sample must be used in both cases, and no more reagent or mounting media should be used than is necessary to hold the cover-glass without any air being impinged. The same microscope and objectives, as well as other conditions, must be employed to secure even *approximate results*, as this is *all that can be expected at present.*

In the examination of low-grade flours when there is no adulteration with corn-meal, it is not possible to obtain quantitative values, save in terms of some other samples, the market value of which and the extent of refining are known. In the consideration of samples of flour containing corn-meal we find a different

condition. Here the quantitative valuation in terms of corn-meal is based upon the comparison of the unknown samples with prepared samples containing a definite percentage of corn-meal. The count is based upon the number of typical angular corn starch grains with prominent fissures found in the five places of each of twelve mounts, as indicated in Fig. 2. Samples of flour containing from five to ten per cent. of corn-meal have on the average from two to three typical corn starch grains in each mount. When the adulteration varies from ten to twelve per cent. the average number of these starch grains is increased from four to six. In samples containing twenty-five per cent. of corn-meal the average number of typical grains increases to seven, etc., but as the adulteration of commercial flours, according to the author's experience, does not exceed ten to twenty per cent., it is not necessary to proceed further in this direction.

CLASSIFICATION.

From the results of the following experiments a classification of the commercial flours may be made as follows:

I. Those that produce a stiff and cohesive dough in the proportion of fourteen to fifteen grams of flour to ten cc. of water; as, for example, a good spring wheat flour.

II. Those that do not produce a stiff and cohesive dough in the proportion of fourteen to fifteen grams of flour to ten cc. of water.

These may be further divided into the following subclasses:

A. Those that form a smooth, jelly-like paste upon boiling one gram of flour with fifteen cc. of water for about one minute; as, good winter wheat and some of the blended flours.

B. Those in which a more or less granular or liquid paste results. This subclass may be further sub-divided into:

(*a*) Those which give off an odor of roasting corn when heated in glycerin to boiling for a few minutes, as samples containing corn-meal.

(*b*) Those that do not give off an odor of roasted corn when heated to boiling with glycerin, as lower grades of flour.

The quality of these flours may be still further determined by a microscopic examination of either the flour or the gluten mass

after removal of the starch, when the presence of fungi and other foreign substances are revealed.

It appears that in certain sections of the country the adulteration of flour, as of other powdered commercial products, is still practiced, yet it may be said that as a rule the article as found in the eastern markets, represents a higher grade of product than has formerly been reported.

The investigations of the writer indicate certain profitable lines of work which are of immediate practical value, and it must be said that much still remains to be done, particularly in the micro-physical examination of the different starches; and the author is of the opinion that as much useful knowledge will be secured by the utilization of the polariscope in this field of work, as has already been disclosed by other methods, the usefulness of this instrument having been demonstrated in the examination of the products made from plant and other fibers.

The author is indebted to Professor Higley, of Northwestern University, and to J. W. Dietrich, of Galesburg, Mo., for assistance in procuring samples; and to Miss Florence Yaple, of the Philadelphia College of Pharmacy, for the performance of much experimental work in the course of the investigation.

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PREPARATION OF GRAPHITOIDAL SILICON.[1]

BY FREDERICK S. HYDE.

Received April 12, 1899.

THE analogy between silicon and carbon in their allotropic modifications, especially the graphitic, and the existence of a crystalline compound of silicon and carbon, known as carborundum, have tended to create doubt as to the purity of graphitoidal silicon, yet the production of the latter seems to be based on reactions favoring the exclusion of carbon.

The usual methods involve the reduction of potassium-silicofluoride with aluminum or metallic sodium; or the reduction of pulverized white sand with magnesium powder.

The method submitted depends on the reduction of finely pul-

[1] Read at the meeting of the New York Section of the American Chemical Society, March 10, 1899.

verized white sand with magnesium powder and the subsequent fusion of the reduction-product with cryolite and aluminum, to form an alloy of aluminum and silicon, from which the latter is obtained on treatment with hydrochloric acid.

For experiment take :

	Grams.
Finely pulverized white sand	12
Magnesium powder	3

Mix thoroughly, place in a dry test-tube, supported by a clamp on a ring stand, warm gently, and then commencing at the lower end ignite cautiously with the burner in hand.

There may be a slight separation of the contents due to the expansion of air or moisture, which should be remedied. As the heat becomes concentrated at the lower end, the contents become darker, resulting in a quiet incandescence which creeps toward the upper part, usually completing the reaction with a slight puff. The exterior surface of the test-tube assumes a greenish black lustrous appearance and becomes wrinkled or "buckled" from the heat of the reaction. Remove the contents, which are brownish black in color ; pulverize and mix with a sufficient quantity of cryolite powder.

Introduce the mixture into a small Denver crucible, containing a piece of aluminum (walnut size) on the bottom. The cryolite serves as a vehicle for incorporating the reduction product with the aluminum and as a flux for impurities. Place the crucible in a small gas furnace and apply blast.

As soon as the aluminum liquefies, stir the mass thoroughly with an iron rod. Quite a little stirring is necessary in order that the molten aluminum may be brought into contact with every portion of the reduced mass. Near the final stage, fumes and tongues of bluish flame, like burning zinc, may be observed on the surface. Allow to cool.

Remove the regulus, which should have a brilliant silver-white crystalline surface, and examine the blackened slag for any small globules of alloy. Place the regulus and globules in a porcelain dish or casserole, and treat with warm hydrochloric acid. As the aluminum dissolves, black glistening spangles of silicon separate out of the solution. Decant and wash with clear water. Then wash with alcohol and dry on the filter.

Some employ zinc to form the alloy, but aluminum is preferable for the following reasons not stated in the text-books:

First.—Zinc melts and volatilizes at a comparatively low temperature, before the silicon has a chance to become properly alloyed. It is also difficult to combine the reaction-product with molten zinc, since the latter is heavier and causes the former to float.

Second.—The copious white fumes and blue flame evolved by zinc, even though the crucible be covered and the oxidation minimized, cause large amounts of "zinc wool" to condense on the interior of furnace and crucible, thus interfering with the operation.

Third.—The zinc-silicon alloy is hard and resists solution with hot or cold hydrochloric acid, while the aluminum alloy is readily dissolved.

Fourth.—Zinc tends to produce needle-shaped crystals of silicon, which are not so striking as the graphitoidal spangles obtained from the aluminum alloy.

Graphitoidal silicon resists oxidation before the blowpipe. Under the microscope, by reflected light, the faces of incomplete octahedra are visible in the small irregularly shaped masses. The yield is rarely more than ten per cent. by weight of the silica employed.

There are indications that the element silicon itself, heretofore classed among laboratory curiosities, may become commercially important.

On account of its high electrical resistance, its use in the form of compact rods has already been suggested for electric heating apparatus.

THE COMPARATIVE VALUE OF CERTAIN REAGENTS FOR REMOVING LIME AND MAGNESIA FROM NATURAL WATERS FOR INDUSTRIAL USES.[1]

BY MARTIN L. GRIFFIN.

Received May 8, 1899.

IT is only within the past few years, fifteen to twenty possibly, that the purification of water mechanically and chemically has claimed the serious attention of engineers and chemists. Everything is done on such a vast scale to-day and competition is

[1] Read at the meeting of the New York Section of the American Chemical Society, May 5, 1899.

so great that things which were counted of little consequence a few years ago may determine success or failure now. Water contained the same impurities a thousand years ago as it does to-day, but they did not play the same rôle. We all remember when every house had a cistern to catch the pure rain-water from the clouds, when industries sought the source of pure water for their uses. It is the common practice of cities to-day to do this, though there are conspicuous exceptions where extensive filtration and purifying plants are being constructed. Formerly paper-mills were in the habit of digging wells or arching over large areas in the beds of streams and canals in order to obtain a pure water supply. Sponges were used as a filtering medium. Fifteen years ago the company which I continue to serve purified its water for making chemical fiber by pumping the water through a mass of excelsior, which at frequent intervals gave way and passed into the pulp to the confusion of the superintendent, who at first concluded that he had a "bad cook."

These inadequate and unscientific practices are fast giving way to scientific and efficient processes. In 1883 and 1884 J. W. Hyatt and Isaiah Smith Hyatt brought out the modern system of filtration and were the first to claim the use of a coagulant for the precipitation of organic matter in water. One would think that soluble organic matter as it naturally occurs in surface waters would be the most difficult of removal, but with the modern filter using a coagulant this is now accomplished beautifully, leaving nothing to be desired. If we could precipitate and filter out the lime, magnesia, and sulphuric acid as completely as we can remove organic matter, there would be little work remaining for the chemist to investigate in this direction. This, no doubt, has been a favorite theme for speculation with many chemists ; however, our inability to do this completely should not prevent putting forth our best endeavors to render a valuable service.

In 1882, Dr. C. B. Dudley obtained a patent for a process using caustic soda for purifying water, claiming as a result that "the lime and magnesia separate as carbonates and the iron and alumina probably as hydrated oxides, etc." This statement assumes that the lime and magnesia exist as bicarbonates only and leaves the subject vague and indefinite.

In 1883 the same author obtained a patent for the use of soda-lime for similar purposes, stating the result of the whole operation to be, "that by far the largest part of the mineral impurities existing in the water previous to treatment are removed."

Doubtless the failure to accomplish all that was expected of this process brought out another claim by Dr. Dudley the next year, which is in effect an amendment to the soda-lime process. In this he adds the use of barium hydroxide, and states that "the result of the whole operation will be that nearly all the mineral impurities occurring in the water, including the sulphuric acid, will be removed from it."

At the first general meeting of this society held in Newport, R. I., in 1890, and which I had the pleasure of attending, Dr. Chas. A. Doremus presented a short paper calling attention to the use of fluoride, particularly sodium fluoride for softening hard waters. At that time the most important statement made was that "the precipitation of magnesium is especially thorough and noteworthy."

In 1893 the same author directed the attention of chemists again to the same subject, perhaps laying more stress on the ability of sodium fluoride to prevent incrustation in feed waters. This statement also appears: "When sodium fluoride is added to waters containing even a moderate proportion of calcium and magnesium salts, a precipitate forms at once." In his patent covering the use of this chemical process, he says: "Since the character of the precipitate produced by a fluoride may be such that it is difficult for a filter to separate it from the water, it may prove advisable to use with the fluoride some chemical capable of producing with the foreign substance in the water a bulky precipitate which shall act mechanically in removing any precipitate of fluoride also produced. Since magnesium fluoride is precipitated in a more flocculent form than calcium fluoride, water containing much magnesium salts may be treated effectually with the fluoride alone, etc. Since caustic soda causes a bulky precipitate when added to waters containing calcium salts, it may be employed with a fluoride for the above-mentioned purpose."

He also says that he has found the use of carbonate and caustic soda with a fluoride more serviceable with certain waters

than when the fluoride alone was used, and that "highly carbonated waters especially seemed to require the use of some caustic alkali." I call attention to these statements, as there seems to be a lack of harmony with the claims made for fluoride. We shall also see that caustic soda in waters containing only calcium sulphate, unless in unusually large amounts, produces no precipitate whatever, and that waters highly charged with carbonates are best suited for the fluoride treatment because of the easy reaction. It was not until I received the January number of the Journal this year, containing an article on "Sodium Aluminate as a Means for the Removal of Lime and Suspended Matter from Waters for use in Boilers," by Prof. Mabery and Edwin B. Baltzley, that I determined to make a systematic quantitative investigation into the value of these and other reagents for removing lime and magnesia from natural waters.

Their method is based on certain reactions which the authors give, all depending on the presence of calcium or magnesium bicarbonate in the waters at the beginning and giving calcium and magnesium carbonates as a final result of the reaction, including the precipitation of the alumina as hydrate.

In regard to waters which contain no carbonates, as for instance, a certain well in Ashtabula, Ohio, cited by the authors, their explanation does not apply. But this is not important. We know that the results depend upon the relative affinities of the bases and acids entering into the reactions and the insolubility of the resulting calcium and magnesium salts.

The authors state that they have made a test comparing the use of different proportions of caustic soda, with aluminate, with the result that "the removal of lime was not much more than half the quantity taken out by aluminate, and the magnesia was not affected." This is certainly a result which chemists could not reasonably expect. The use of sodium aluminate for such purposes is only another way of introducing the strong base sodium, since nothing can be claimed for the precipitated alumina except for its mechanical action. We would therefore look for the same kind of an action whether we were to use sodium hydroxide or aluminate, the free base, however, acting more promptly and with greater intensity.

Also in the case of waters containing only calcium and

magnesium sulphates we would have expected better results in the removal of the magnesium than the calcium, since magnesium hydroxide is far more insoluble than calcium hydroxide.

In the case of one sample the authors say that "air was blown through the solution for a few minutes." No explanation is given for this. Out of some seven samples of water treated, over ninety per cent. of the calcium and magnesium were reported removed from six of them, while the remaining sample, though only an ordinary river-water, gave "unsatisfactory results." It seems that some explanation should have been given for this. The practicability of the process is beyond the scope of this paper.

The reagents selected for my investigation were sodium hydroxide, sodium phosphate, sodium fluoride, sodium aluminate, and barium hydroxide. It will be observed that the primary intent in this work is to introduce a strong, free base, throwing down the insoluble carbonates and hydroxides, of which iron, aluminum, and magnesium are quite insoluble, while that of calcium is easily soluble. We might pause if it were not for this solubility of calcium hydroxide, but unfortunately again the calcium salts are the principal mineral impurities in natural waters, so we pursue our search for a reagent possessing a very strong base and an acid having a greater affinity for the bases calcium and magnesium, and whose salts are insoluble, and we include sodium phosphate and fluoride.

With regard to sodium aluminate, this may be classed with the free base inasmuch as the alumina acts as a very weak acid. I have included it in the test in consequence of the claims made for it by the authors. The principal precipitates resulting from the use of these five reagents are calcium and magnesium carbonates, phosphates, fluorides and hydroxide, iron and aluminum hydroxides, and barium sulphate. With the exception of magnesium phosphate and calcium hydroxide, they are among the most insoluble precipitates we have, but the greater solubility of freshly made precipitates and the greater inactivity of reagents in weak solutions are obstacles to success. The relative affinities also play an important rôle.

The experiments were conducted upon a half liter of water usually, and the results are given in fractions of a gram per

liter. Those who desire to read the results in grains per United States gallon (231 cu. in.), may use the factor 58.38, and for the Imperial gallon ($277\frac{1}{4}$ cubic inches) the factor 70. The half liter of the water at the ordinary atmospheric temperature was transferred to a flask of double the capacity, when a slight excess of the reagent to be employed was introduced. The whole was shaken, corked, and allowed to stand on an average of one or two days. The water was then filtered through a close, heavy paper S. S. 598 and the lime and magnesia in solution determined. The reagents employed were normal solutions of sodium hydroxide and fluoride and tenth-normal sodium phosphate and barium hydroxide. The aluminate solution was prepared from a pure aluminum sulphate containing 56.68 per cent. anhydrous sulphate, ten grams to the liter, to which sodium hydroxide was added to alkaline reaction.

In order to obtain some idea of what to expect I began the work with simple solutions of calcium and magnesium. The first was a solution of calcium sulphate containing 0.072 gram calcium oxide, and there remained after treatment with

	Hours.	Calcium oxide. Gram.
Aluminate solution	46	0.060
Sodium hydroxide	76	No precipitate
Barium hydroxide	40	0.060
Sodium phosphate	48	0.032
Sodium fluoride	28	0.014

Here we observe that all reagents producing the hydroxides are unsatisfactory, while the best results are obtained with the fluoride.

Next a solution of magnesium sulphate containing 0.061 gram magnesium oxide was taken, and there remained in solution after treatment with

	Hours.	Magnesium oxide. Gram.
Aluminate solution	25	0.0115
Sodium hydroxide	27	0.0349
Barium hydroxide	21	0.0183
Sodium phosphate	44	No precipitate
Sodium fluoride	26	" "

In this case we see that the reagents producing hydroxides are much more successful.

A solution of magnesium chloride containing 0.0558 gram magnesium oxide contained after treatment with

	Hours.	Magnesium oxide. Gram.
Aluminate solution	17	0.0082
Sodium hydroxide	17	0.018
Barium hydroxide	12	No precipitate
Sodium phosphate	120	" "
Sodium fluoride	28	" "

The latter was concentrated by boiling to one-fifth the original bulk and still no precipitate appeared, showing that no reaction could take place. In this instance only the aluminate and caustic gave results, the former doing particularly well.

We now pass to some natural waters. A sample from the Hudson River at Mechanicsville contains

	Gram.		Gram.
Calcium carbonate	0.0234	equivalent calcium oxide	0.0176
" sulphate	0.0110		
Magnesium carbonate	0.0102	" magnesium "	0.0050

and there remained after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	46	0.0180	0.0048
Sodium hydroxide	42	0.0160	0.0043
Barium hydroxide	21	0.0176	0.0046
Sodium phosphate	24	No precipitate.	
Sodium fluoride	24	" "	

In this case none of the reagents were able to effect any appreciable reduction in the amounts of lime and magnesia.

The next is a sample from the middle of Lake Champlain opposite Ticonderoga, and contains somewhat more lime and magnesia, though it is not a hard water. It contains

	Gram.		Gram.
Calcium carbonate	0.0341	equivalent calcium oxide	0.0255
" sulphate	0.0156		
Magnesium carbonate	0.0147	" magnesium "	0.0070

and there remained after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	47	0.0256	0.0068
Sodium hydroxide	25	0.0256	0.0064
Barium hydroxide	25	0.0260	0.0060
Sodium fluoride	47	0.0250	0.0057

We draw the same conclusions here as in the case of the Hudson River water.

The next is a sample of tap-water from the city of Niagara Falls and is the Niagara River water. It contains

	Gram.		Gram.
Calcium carbonate	0.0332	equivalent calcium oxide	0.0448
" sulphate	0.0640		
Magnesium carbonate	0.0272	" magnesium "	0.0129

and there remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	45	0.0260	0.0118
Sodium hydroxide	46	0.0100	0.0057
Barium hydroxide	45	0.0430	0.0100
Sodium fluoride	46	0.0190	0.0130

We observe that sodium hydroxide gives the best results with fluoride second.

The next sample is from a driven well in Mechanicsville which I will call B. It contains

	Gram.		Gram.
Calcium carbonate	0.0620	equivalent calcium oxide	0.0760
" sulphate	0.1003		
Magnesium carbonate	0.0552	" magnesium "	0.0263

and there remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	18	0.0650	0.0237
Sodium hydroxide	17	0.0160	0.0147
Barium hydroxide	24	0.0260	0.0150
Sodium phosphate	17	0.0650	0.0240
Sodium fluoride	46	0.0270	0.0234

Sodium and barium hydroxide give the best results with this water.

The following is also from a local well which I will call D. It contains

	Gram.		Gram.
Calcium carbonate	0.0398	equivalent calcium oxide	0.0940
" sulphate	0.1760		
Magnesium carbonate	0.0703	" magnesium "	0.0330

There remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	24	0.080	0.0236
Sodium hydroxide	27	0.022	0.0133
Barium hydroxide	24	0.063	0.0029
Sodium phosphate	17	0.068	0.0273
Sodium fluoride	71	0.035	0.0338

Again we observe that the best results are obtained with sodium hydroxide, with sodium fluoride second in reference to lime, and barium hydroxide second when we include magnesia.

The next sample is from the Chazy Marble Lime Co.'s quarries in northern New York, and is used in their boilers. It contains

	Gram.		Gram.
Calcium carbonate	0.1100	equivalent calcium oxide	0.0850
" sulphate	0.0570		
Magnesium carbonate	0.0323	" magnesium "	0.0154

There remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	63	0.0670	0.0136
Sodium hydroxide	40	0.0150	0.0111
Barium hydroxide	41	0.0240	0.0115
Sodium fluoride	40	0.0170	0.0115

In this case sodium hydroxide and sodium fluoride gave nearly equally good results.

The following sample is from a well fourteen feet in solid rock near Lake Champlain in Chazy, N. Y. It contains

	Gram.		Gram.
Calcium carbonate	0.1818	equivalent calcium oxide	0.1140
" sulphate	0.0148		
Magnesium carbonate	0.0520	" magnesium "	0.0248

and contained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	88	0.0720	0.0208
Sodium hydroxide	42	0.0140	0.0186
Barium hydroxide	40	0.0300	0.0146
Sodium fluoride	42	0.0220	0.0172

Three out of the four reagents gave very satisfactory results.

The next is a sample of mine water from the Coxe Iron Mfg. Co., at Drifton, Pa., and contains

	Gram.			Gram.
Ferrous sulphate	0.0440	equivalent ferrous oxide		0.0208
Calcium sulphate	0.0534	" calcium	"	0.0220
Magnesium sulphate	0.1554	" magnesium	"	0.0518
Free sulphuric acid	0.1450			

and there remained in solution after treatment with

	Hours.	Ferrous oxide. Gram.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	71	trace	0.0200	0.0516
Sodium hydroxide	16	none	0.0220	none
Barium hydroxide	16	"	0.0220	0.0064
Sodium fluoride	112	No trace of any precipitate		

showing that this reagent was of no use. The sulphuric acid was not determined. We notice that sodium and barium hydroxide gave very satisfactory results. Barium hydroxide would doubtless be preferred, as it would largely remove the sulphuric acid.

The following sample is from the mouth of Onondaga Creek, Syracuse, N. Y., and contains

	Gram.			
Total solids	1.6200			
Sodium chloride	0.6550			
Magnesium chloride	0.0254	equivalent magnesium oxide		0.0298
" carbonate	0.0493			
Calcium sulphate	0.2176	" calcium	"	0.3480
" carbonate	0.4614			

and contained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	98	0.0840	0.0014
Sodium hydroxide	17	0.1280	0.0043
Barium hydroxide	136	0.0260	0.0028
Sodium fluoride	117	0.0420	0.0288

In this case barium hydroxide gave the best results, with sodium fluoride second, in reference to lime.

The last sample is from the magnesian lime quarries of the Snow Flake Lime Co., Bowling Green, Ohio, and contains

	Gram.		Gram.
Calcium carbonate	0.0870 }	equivalent calcium oxide	0.2080
" sulphate	0.3868 }		
Magnesium carbonate.	0.1662	" magnesium "	0.0792

and contained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution.....	63	0.0080	none
Sodium hydroxide.....	16	0.0090	0.0018
Barium hydroxide	16	0.0680	0.0064
Sodium fluoride	21	0.0250	0.0597

In this case we obtain the best results with the aluminate, but the treatment with sodium hydroxide follows so closely that practically there is little difference. The use of barium hydroxide and sodium fluoride are not so satisfactory.

In this work I have endeavored to get samples of characteristic and representative natural waters, such as are commonly met with in the industries, and think the ground is fairly well covered, so that the deductions to be made shall be true and useful.

We note first the limit to which we are able to purify waters in this way, and within what limits we are able to effect a reduction in the amount of earthy substances, by the use of any of the above reagents. The Hudson River contains 0.0176 gram calcium oxide and 0.005 gram magnesium oxide. These amounts we cannot reduce. Lake Champlain, containing 0.0255 gram calcium oxide and 0.007 gram magnesium oxide, could not be reduced, but increasing amounts above these figures show a reduction by one or more of the reagents. I conclude, therefore, that waters containing from 0.020 to 0.025 gram calcium oxide and from 0.005 to 0.007 gram magnesium oxide cannot be purified appreciably, although we observe that frequently the amounts of these impurities can be reduced below these limits in the case of waters highly charged, which is a favorable feature of the work. As regards the removal of calcium carbonate, the most effectual reagents are sodium hydroxide and sodium fluoride, and in some cases we observe that the aluminate solution gave particularly good results as in the last sample, but I will refer to this again. The best results show a reduction in the amounts of calcium oxide of 0.008 to 0.010 gram. It appears also that waters containing a large propor-

tion of calcium sulphate with carbonate can be successfully treated with these reagents as in the case of limestone quarry waters. Barium hydroxide did not prove as effective as I anticipated in the removal of lime.

As regards the removal of magnesium salts, we observe again that sodium hydroxide averages best, with barium hydroxide following very closely, while aluminate solution takes third place, and sodium fluoride produces practically no results on any of the samples. Sodium phosphate was so unpromising from the start, and the removal of the phosphoric acid from the water after treatment added so much to the labor of the work, that I abandoned its use.

We cannot conclude, however, that sodium hydroxide is the best reagent for all waters. Sodium fluoride is much to be preferred in waters containing calcium sulphate and chloride, and is of no value in the removal of magnesium salts.

Barium hydroxide is most serviceable in the treatment of acid mine waters and gave very satisfactory results in the case of Onondaga Creek water, the character of which may be seen from the analysis:

Referring back to the references in the early part of this paper, we are able to place definite limits to Dr. Dudley's processes and to know how far they may be useful. Dr. Doremus' claims for sodium fluoride for the precipitation of calcium salts are fairly well established, but for the precipitation of magnesium salts it is a failure, and for the removal of iron and magnesium very questionable. In my experiments with sodium aluminate I endeavored to follow the suggestions of Prof. Mabery, using somewhat less than the theoretical amount of the combined sodium oxide (Na_2O) in the aluminate necessary to replace the bases lime and magnesia, although the reason for doing this is not plain to me. In every case the action of the aluminate was comparatively slow, and in the case of the lime salts did not give satisfactory results or meet the claims of its authors. It proved more effectual in the removal of magnesium salts, which was to be expected.

I desire to refer to the composition of the aluminate reagent before the subject is left. I prepared this reagent as Prof. Mabery directs, from sodium hydroxide and aluminum sulphate,

	Originally.		Aluminate.		N,NaOH.		$\frac{N}{10}Ba(OH)_2$.		N,NaFl.		$\frac{N}{10}Na_2HPO_4$.	
	CaO.	MgO.	CaO.	MgO.	CaO.	MgO.	CaO.	MgO.	CaO.	MgO.	CaO.	MgO.
$CaSO_4$ solution	0.0720		0.0580		0.0720		0.0600		0.0140		0.0320	
$MgSO_4$ solution.....		0.0610		0.0115		0.0349		0.0183		0.0610		0.0610
$MgCl_2$ solution		0.0558		0.0082		0.0180		0.0558		0.0558		0.0558
Hudson River		0.0050		0.0048		0.0043		0.0046		0.0050		0.0050
	0.0176		0.0180		0.0160		0.0176		0.0176		0.0176	
Lake Champlain		0.0070		0.0068		0.0064		0.0060		0.0057		
	0.0255		0.0256		0.0256		0.0260		0.0250			
Niagara River.....		0.0129		0.0118		0.0057		0.0100		0.0130		
	0.0448		0.0260		0.0100		0.0430		0.0190			
Well B		0.0263		0.0237		0.0147		0.0150		0.0234		0.0240
	0.0760		0.0650		0.0160		0.0260		0.0270		0.0650	
Well D		0.0334		0.0236		0.0133		0.0029		0.0338		0.0273
	0.0940		0.0800		0.0220		0.0630		0.0350		0.0680	
Chazy Quarry		0.0150		0.0136		0.0111		0.0115		0.0115		
	0.0850		0.0670		0.0150		0.0240		0.0170			
Chazy Well.....		0.0248		0.0208		0.0186		0.0146		0.0172		
	0.1140		0.0720		0.0140		0.0300		0.0220			
Coxe Mine.....		0.0518		0.0516		0.0000		0.0064		0.0518		
	0.0220		0.0200		0.0220		0.0220		0.0220			
Onondaga Creek		0.0298		0.0014		0.0043		0.0028		0.0288		
	0.3480		0.0840		0.1280		0.0260		0.0420			
Bowling Green.....		0.0792		0.0000		0.0018		0.0064		0.0597		
	0.2080		0.0080		0.0090		0.0680		0.0250			

from which it will be seen that the available sodium oxide in combination with the alumina is but a small proportion of the composition of the reagent, there being three inert molecules of sodium sulphate to one of sodium oxide beside the alumina. I have no doubt this exerted some influence on the sample of water to which the reagent was added in causing a more complete precipitate of lime and magnesia in some cases.

It would be better to prepare this reagent from pure alumina and sodium hydroxide. As it is, the results are comparable with those reported by Prof. Mabery.

If this reagent could be made as effective in simple practice as the authors claim, leaving practically no alumina in the filtered water, its discovery would prove to be of immense value at once.

In conclusion I would say that there is little doubt but that satisfactory reagents and means will soon be discovered whereby all objectionable waters may be successfully treated at comparatively small expense.

Later I may have something further to contribute to this end.

REVIEW.

THE RETORT COKE OVEN AND THE CHEMISTRY OF ITS BY-PRODUCTS.

There is no innovation into the realm of metallurgical science, these last days of the nineteenth century, which will affect more widely and will, one might say, so revolutionize the whole system of iron- and steel-making in this country as will the introduction of the retort oven for the production of coke, with the simultaneous recovery of the by-products, tar, ammonia, benzene, cyanides and illuminating and fuel gas.

Think of the devastation in the beehive coke oven districts for the year 1897. One has only to take the government statistics of the coke manufactured in this country for 1897 and put opposite it the coke to be made from the same coal in retort ovens of the Semet-Solvay type together with the long list of valuable by-products obtainable, to see the vast amount of valuable material destroyed annually by the present system of coking coal in beehive ovens, and to realize the extent to which humanity has been deprived of what rightly belongs to it. The figures below will illustrate what was actually obtained from the beehive coke ovens in the United States from 22,140,000 tons of

coal in the year 1897, and what would have been obtained if the same coal had been coked in retort ovens:

	Beehive ovens.	By-product ovens.
Tons coal coked	22,140,000	22,140,000
Tons coke produced	13,288,984	15,940,000
Value of coke at $2 per ton	$26,577,968	$31,880,000
Value of tar	.....	4,428,000
Value of ammonia	.....	8,856,000
Value of cyanides	.....	8,020,000
Value of benzene	.....	4,428,000
Value of gas (surplus), 22,140,000 × 4000 = 88,560,000,000 cubic feet at 10 cts	.....	8,856,000
Total	$26,577,968	$66,468,000

Difference in favor of by-product ovens $39,890,032.

It will be seen by these figures that the saving in coke alone is over 2,600,000 tons, having a value of over $5,000,000.

These comparisons are made to enable one to comprehend more clearly the immense waste coexistent with the production of coke by the beehive process. The fact is duly appreciated that should all, or a considerable portion, of the coke now made in beehive ovens become the product of retort ovens, the price of the by-products would be greatly diminished.

It will not be long ere the most important blast-furnaces and steel plants throughout the country will be supplied with their own by-product coke ovens, the coke going directly from the quenching car to the blast-furnace without handling, and the surplus gas being used for heating the various furnaces in the steel plant.

Natural gas is giving out. The people, having become accustomed to its conveniences will never go back to the use of coal. They must have a gaseous fuel as a substitute for natural gas.

Boards of health and sanitary organizations are crying out continually against the filthy and unhealthy condition of our cities, arising from the consumption of so much soft coal. There is no longer any comfort in a home in or near a manufacturing city. Travel on steam trains is almost unbearable in certain seasons because of smoke and soot from the engine. What is the remedy? It is the retort coke oven. Retort ovens in the future will also be built in the vicinity of large cities for the production of domestic coke and illuminating gas. Not only will fuel gas be furnished at very low figures, but illuminating gas will be sold at twenty cents per thousand. No smoke will be seen issuing from chimneys and polluting the city and country for miles about, but coke will be the fuel unless gas is used. Stationary steam engines will be a thing of the past, and gas engines up to 1000 H.P. will be substituted, with less cost for power, on account of the low price of fuel gas. Traveling will

be a pleasure for coke will be used in the locomotive, in the place of bituminous coal. But what is to be done with the huge amount of tar recovered? As the production of tar increases, the price must necessarily fall and the lower price will extend the field of consumption. It is only a question of further experimentation and research to successfully incorporate pitch into pavements ; lowering the price of "dead oil" will increase the amount of creosoting of timber; there is always the value of tar as a fuel. Millions of tons of the anthracite culm of Pennsylvania and the slack of Ohio, which are now of no value, will, before long, be made into briquettes, thereby consuming thousands of tons of pitch.

But what will we do with so much ammonia? This will be a God-send to the farmer, whose fields are now crying for more nitrogen. His barnyards do not furnish enough of it, and fertilizers are now too expensive. His crops are continually drawing on the nitrogen of the soil, and it must be replaced. In England alone, 120,000 tons of nitrogen annually are abstracted from the soil by vegetable growth, wheat absorbing 37,000, barley 27,000, and oats 57,000 tons. This nitrogen, at present, is principally furnished by the niter beds of Chili. This source in time must fail—England's recourse will be to the nitrogen of her coals which will be coked about her large cities, to be no longer shrouded in black clouds of smoke which obscure the noon-day sun and pollute the atmosphere to that extent that many a man is brought to death's door before his time, and others eke out a half-dead and half-alive existence.

The ammonia formed will be converted into ammonium sulphate, which will largely replace sodium nitrate for fertilizer purposes, and in this country the price will be so reduced as to enable the farmer to use large quantities of it.

Cheap domestic coke or fuel gas from coke ovens will be the only salvation for England's large cities.

Liebig certainly was right when he said, first, "In order to preserve the fertility of the soil, there must be kept in that soil the elements necessary for plant life; second, every crop takes out a portion of these elements. Part of that taken out is added again from the atmosphere, but a part never is restored unless it is put there by human means; and third, the fertility of a soil remains unchanged if all the elements of fertility are restored to it; and fourth, the manurial product of a farm never can restore all the elements of fertility to the soil."

Once a plentiful supply of benzene, toluene, etc., is assured in this country, the aniline color manufacturer will succeed.

A cheap and plentiful supply of cyanides will enable mining engineers to work gold fields which now cannot be successfully worked.

HISTORICAL.

It is about fifteen years since the retort coke oven became a factor in the production of metallurgical coke. The now nearly perfect oven is the result of gradual development from very crude and imperfect ones. There are two types of retort ovens, one in which the horizontal flue is the characterizing feature, and of which class the Semet-Solvay oven is the chief exponent; the other type, in which the heating flues are vertical, is represented by the Otto-Hoffman oven. The first Semet-Solvay ovens, six in number, were experimental and built in 1882, near Mons, Belgium. After a trial of two years the practicability of the system was satisfactorily established and more ovens were built annually, and from 1892 the number of Semet-Solvay ovens has greatly increased, so that at the end of 1897, ovens of this system numbered over 1300. The first in this country were built at Syracuse, in 1892, twelve at first, to which thirteen more were added later. These have been running constantly ever since, with slight repairs.

There are at present in operation on this continent of the Semet-Solvay type, 25 ovens at Syracuse, N. Y.; 50 ovens at Dunbar, Penna.; 25 ovens at Sharon, Penna.; 120 ovens at Ensley, Ala.; 60 ovens at Wheeling, W. Va.; 10 ovens at Halifax; 7 ovens at Boston, Mass. The others are distributed throughout Germany, France, England and Belgium, principally in Belgium where they are very successful in coking low volatile coals, which, in the beehive oven, will not make coke.

DESCRIPTION AND OPERATION OF A RETORT COKE OVEN.

A description of a single isolated Semet-Solvay oven would be as follows: A space five feet, six inches high, sixteen to twenty inches wide, and thirty feet long, is enclosed on both sides by hollow fire-brick tile in three tiers superimposed, placed horizontally. These tiles are about three feet long and when placed end to end form a flue through which the gas, after being treated for removal of the by-products, travels and meets the air for combustion.

The gas is admitted at the ends of the top and the second flues, with a suitable amount of air which has been previously heated by the waste gases going to the chimney flue. At one end of each flue is an opening in the bottom through which the gas passes to the next flue below, the gas and flame passing through the entire length of the flues and finally to the chimney flue.

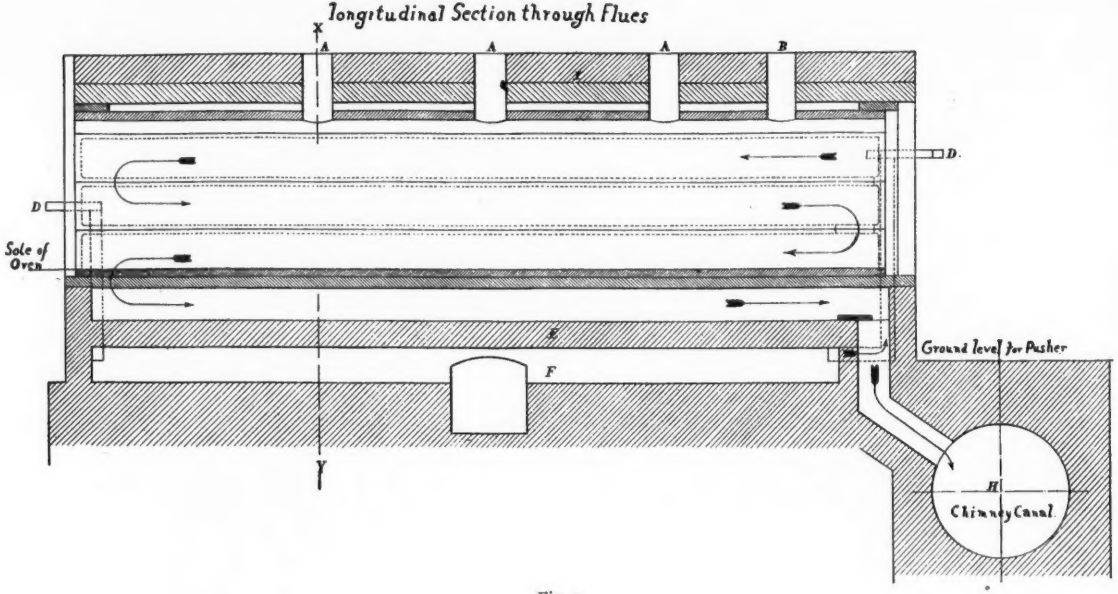
Longitudinal Section through Flues
X
A
A
A
B
D
D
Sole of Oven
E
F
Ground level for Pusher
H
Chimney Canal
Y

Fig. 1.

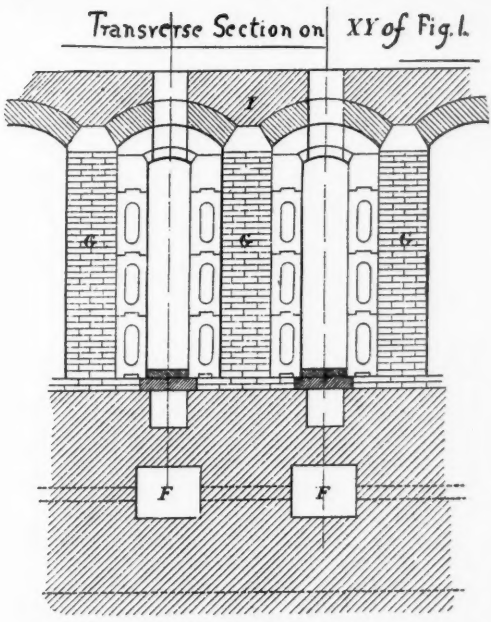

Fig. 2.

The air for combustion is drawn by the chimney draft through a flue, where it is heated by the gases of combustion passing in a flue below the oven, to a temperature of 200°–300° C. The air is admitted and regulated by means of dampers so nicely, and the gas is under such perfect control, that combustion takes place with the minimum amount of air, and the temperature of flues may be maintained as one wishes from 900°–1400° C.

The waste gases, still of about 700°–800° C. temperature, pass under boilers in the by-product plant, which make all the steam necessary to operate all the machinery about the plant, and furnish steam for distillation of the ammonia recovered. From the boilers the waste gases go to the chimney at about 250° C.

The coal, after disintegration, is elevated into bins above the ovens from which, by withdrawal of a slide, coal-cars or "larries" are filled and are then run out on tracks on the top of the ovens and the coal is charged through three holes. One "larry", holding 3,200 lbs. of coal, is charged to each hole. The total charge therefore is 9,600 lbs. of coal to an oven. The time re-

quired for discharging and again filling and closing up is about fifteen minutes.

The coal after being charged in the oven is then leveled off by means of long hoes put through a hole in the top of the doors at each end of the oven. The doors at both ends when closed and plastered up with fire-clay are practically air-tight.

The time required for coking depends upon the quality of the coal, and the width of the oven. Pocahontas coal for instance, containing nineteen per cent. volatile matter, may be coked in twenty hours in a Semet-Solvay oven, sixteen inches wide, whereas, Connellsville coal, containing thirty-two per cent. volatile matter, in the same oven would require twenty-four hours to properly coke it. If the oven is twenty inches wide, six hours more, or thirty hours, are necessary to completely expel the gas from Connellsville coal. It is a fact also that two coals containing the same percentage of volatile matter may require different lengths of time for the expulsion of the gas. Though the percentage of volatile matter is the same in the two coals, this volatile matter is made up of different percentages of oxygen, hydrogen, and carbon, and because of this difference the gas is expelled with greater or less difficulty.

An important feature in the construction of the Semet-Solvay oven is that the hollow tiles forming the walls of the oven are entirely independent of the side walls, made of fire-brick, which carry the huge mass of brickwork, coal-cars, etc., above the oven proper, and thus relieve the tile from all strains and thrusts, which would have a tendency to displace them, causing leaks, which would deleteriously affect the gas and other products. Because of the freedom from burden, the oven sides of the tile may be made much thinner than they otherwise could, resulting advantageously in conducting the heat from the flue where the combustion of the gas takes place to the mass of coal in the oven. The thick side walls and mass of brickwork above serve to hold the heat, giving it up to the oven during the time of discharging and charging, thus preventing any chilling of the oven. An expansion chamber above the oven permits the tile to expand without affecting the main body of brickwork.

The gas leaves the oven under neutral or a very slight back pressure and is drawn by an exhauster through a hydraulic main, similar to that used in gas-works, where it is washed free from dust and is partially cooled.

From the hydraulic main the gas goes to large condensers where the gas is cooled by water to 30°C. From the condensers the blower forces the gas through the washer, or scrubber, where the last traces of ammonia and tar are removed. The gas is now divided, such portion as is necessary going back to the

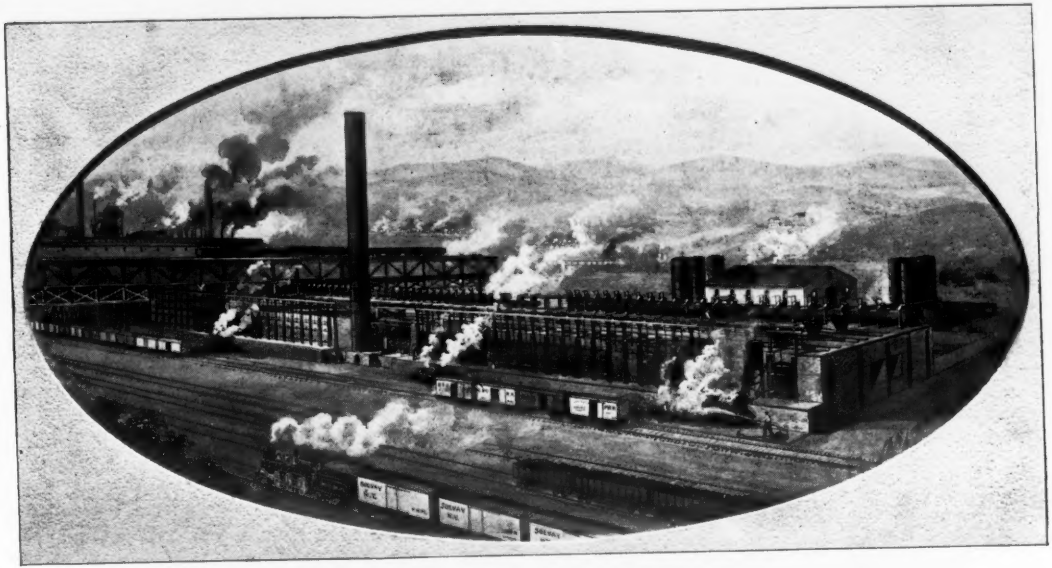

Fig. 3.—Fifty ovens at Dunbar, Pa.

oven flues to keep up the heats, the balance being used wherever fuel may be required.

When the coal is coked, a valve on the uptake pipe shuts off all connection to the hydraulic main; the doors are swung open, or raised, the mechanical ram is put in operation and slowly forces the coke out of the oven, the coke dropping in a thin layer into an inclined car made of iron bars, and a stream of water quenches the coke. The coke holding one and one-half to two and one-half per cent. of water is then elevated for use in lime-kilns or furnaces, or loaded into cars for shipment.

CONTROLLING THE TEMPERATURE OF THE FLUES.

By means of valves on the pipes bringing the gas to the flues for combustion, and by dampers in the air inlets, and by regulation of the chimney draft, any temperature may be obtained, from 900° to 1400° C. The temperatures of the flues are determined by means of the Le Chatelier electrical pyrometer, manufactured by Messrs. Kiser & Schmidt of Berlin, which is a platinum rhodium couple in a porcelain tube which produces a current on exposure to a high temperature and this current is measured by a galvanometer. Another pyrometer which has given good satisfaction is the Callender and Griffiths electrical pyrometer, which depends on the resistance offered by high temperatures to a current from a small battery. Fine platinum wires, through which the current passes, are heated inside a porcelain tube and are in connection with a galvanometer which indicates the temperature. The instrument is favorably spoken of by Lord Kelvin and was used by Messrs. Heycock and Neville in determining the melting-points of gold, silver, and copper.[1]

While these instruments have been found very useful to determine accurately the temperature of the flues, they are too delicate to be left in other hands than the expert. As a substitute the Seger cones enable the foreman or workman to judge very closely of the temperature. A round steel rod, six feet long, with three grooves at the end, each large enough to hold a cone, is thrust through a peep-hole in the end of the flue. After fifteen minutes exposure to the heat the cones are removed and their condition noted.

Another instrument made use of by the foreman in charge of the ovens is the telescopic pyrometer of Messrs. Mesuré & Nouell, which seems especially well adapted for coke oven work. The telescope is directed through the peep-hole against the oven side of the tile, and by the degree of incandescence the temperature is determined. Within the tube of the telescope is a polar-

[1] *Chem. Soc. Trans.*, February, 1895. See also for description: *Phil. Mag.*, July, 1891, and January, 1892. *Journal Iron and Steel Institute*, No. 1, 1892. Also a paper by Profs, Dewar and Flemming: *Phil. Mag.*, 1893.

izer, a piece of quartz, and a decomposer. By rotation of the decomposer when viewing the incandescent object, the color changes from green to red, and between these two a gray-lemon tint is seen. This is the sensible shade and the one to observe. A graduated scale on the disk shows the degrees of rotation; a scale of temperatures corresponding to these degrees is given with the instrument.

By means of this telescopic pyrometer the foreman determines the temperature of the flues, and by proper adjustment of gas, air and draught without difficulty maintains the desired temperatures, which are:

Top flue	800°– 900° C.
Middle flue	1150°–1250° C.
Bottom flue	1050°–1150° C.

COMPARISON OF RETORT COKE AND BEEHIVE COKE.

Because of the widely different conditions under which coke in a by-product oven, and a beehive oven is made, one would naturally expect a difference in the appearance and physical characteristics of the two cokes. The heat stored up in the walls of the retort oven is immediately given up to the coal as it is charged and distillation begins, and proceeds horizontally to the center of the oven, the coal in the center of the oven not reaching a high temperature until the latter part of the time of coking. As a result of this heating from the sides, and a slight swelling or expansion, the coke in a soft state is compressed by the walls slightly, and makes that portion of the coke next the oven wall for about one inch quite dense and of little porosity, while the coke in the center presents a highly cellular appearance, and is more or less spongy; the portion between is hard, dense, and of the customary cellular structure of beehive coke. The coke shrinks away from the oven, thus making it possible for the ram to discharge it; it also separates longitudinally in the center. The thickness of the coke on either side of the center is six and one-half to seven and one-half inches, of which about one and one-half inches is extra dense, and from nothing to one inch in the center is spongy.

The total cellular space of retort coke is practically the same as that of beehive coke, and it is able, because of its strong cellular walls, to bear fully as great a burden in the blast-furnace.

The following table shows determinations of cellular space, specific gravity, etc., of coke made from Connellsville coal in Semet-Solvay ovens, and for comparison are given similar tests of beehive coke for the same coal. It will be seen that cubes taken from that part of the coke near the oven wall contain less percentage of cells and have greater weight per cubic foot than any other part of the coke. The average determinations of the cubes

taken from the center portion of the piece of coke do not vary greatly from the standard Connellsville coke.

The following is a table of physical tests arranged according to Mr. Fulton's plan:

	Grams in one cubic inch.		Pounds in one cubic foot.		Percentage by Volume.		True Sp. Gr.
	Dry.	Wet.	Dry.	Wet.	Coke.	Cells.	
Standard Connellsville Beehive.							
	12.51	21.62	47.69	82.20	43.93	56.07	17.4
Connellsville Semet-Solvay Ovens.							
Outside piece..	14.39	23.27	52.47	88.64	52.47	47.53	1.87
"	18.57	25.32	70.71	96.31	59.85	40.15	1.84
Average,	16.48	24.29	61.59	92.47	56.16	43.84	1.85
Center piece...	12.55	20.81	46.17	79.24	45.88	54.12	1.79
"	15.02	23.09	57.19	87.90	50.47	49.57	1.83
"	15.95	25.27	60.85	97.01	47.09	52.91	1.88
"	15.18	24.87	57.81	94.66	45.31	54.69	1.89
"	14.97	23.32	57.00	88.78	49.30	50.70	1.84
Average,	14.92	23.47	55.8	89.51	47.61	52.39	1.84
Connellsville Beehive.							
No. 1.....	11.93	21.18	45.41	80.61	42.57	57.49	1.74
No. 2.....	14.00	24.16	53.30	91.98	43.39	56.61	1.80
No. 3.....	15.07	24.61	57.37	93.70	45.82	54.18	1.80
Average,	13.66	23.31	52.02	88.72	43.92	56.09	1.78

While distillation in the retort oven proceeds horizontally from the outside to the center, in the beehive oven distillation begins at the top and proceeds vertically, and the coke resulting is taken out in long, slender pieces, whereas the product from retort ovens is in large square chunks.

SIR LOWTHIAN BELL'S EXPERIMENTS.

Many years ago, when the first retort coke was put on the market in England, Sir Lowthian Bell made some experiments by which he proved that retort coke would not answer for blast-furnaces; because of the soft nature of the coke the ascending carbon dioxide in the furnace would be converted to carbon monoxide by the carbon, thus diminishing the quantity of carbon which would reach the lower point in the furnace where it was to do its work. It is true that his experiments did show a considerable conversion of carbon dioxide to carbon monoxide when hot carbon dioxide was passed over retort coke in a glass tube. The coke he used, made in a Simon Carvé oven, was certainly in no respect similar to that now made in the Semet-Solvay ovens, for we have many times repeated Sir Lowthian Bell's experiments, using retort coke from Connellsville coal, and for comparison with it have experimented with the standard Connells-

ville coke, and have obtained practically the same results with both cokes. The following are some of these results:

Ten grams of the coke, size of mustard seed, was placed in a combustion tube and then in a furnace and heated at a red heat for one hour. During this time five liters of dry carbon dioxide was passed over the incandescent coke. At the end of the experiment the coke was again carefully weighed and the loss in weight determined with the following results:

SOLVAY COKE.

	Loss of carbon. Per cent.
Experiment No. 1	0.55
" " 2	0.35
Average	0.45

BEEHIVE COKE.

Experiment No. 3	0.46
" " 4	0.49
Average	0.47

It will thus be seen that the two cokes, as far as the action of the hot carbon dioxide is concerned, are practically the same.

Tests were also made of retort coke and beehive coke from Buffalo, Rochester and Pittsburg coal. Average samples were used in both cases.

By these tests it will be seen that there was less conversion of carbon dioxide to carbon monoxide with the retort coke than with the beehive coke.

CARBON DIOXIDE COKE TEST.

Kind of coke.	Weight used. Grams.	Temperature °C.	Time. Hours.	Volume CO_2. cc.	CO obtained. cc.	CO per 1000 gms. coke. cc.
Beehive, B. R. & P.	13	900° C.	4	3400	15.66	1205
Retort, B. R. & P..	13	900° C.	4	3400	14.78	1137
Beehive, B. R. & P.	25	900° C.	4	3500	29.0	1160
Retort, B. R. & P..	25	900° C.	4	3500	24.0	960

A trial of 1000 tons of retort coke, made from Connellsville coal, coked in the Semet-Solvay ovens at Syracuse, was made at the Buffalo blast-furnace in the summer of 1895, and was reported upon by John Fulton, M. E. This test showed that as good results could be obtained with this coke as with the best standard Connelsville coke.

The blast-furnace at Dunbar, Penna., has used 160 tons of retort or by-product coke per day for the past three years; the furnace at Sharon, Penna., 80 tons; and for the past year the Ensley furnaces have been consuming 360 tons, and an oven plant at Wheeling has been furnishing 180 tons to furnaces in

that locality. It will thus be seen that the successful substitution of retort coke for beehive coke in the blast-furnace is no longer an experiment.

As a foundry coke, that made at Syracuse in the Semet-Solvay ovens is much sought after by the foundrymen, who are willing to pay twenty-five cents more per ton for the retort coke than for the beehive coke.

Foundry coke made in by-product ovens in England sells for two to three shillings more per ton than coke made from the same coal in beehive ovens by the same firm.

A test in a Pittsburg foundry of by-product coke, made from Pittsburg coal, showed that it did over twenty-five per cent. more work than the best beehive Connellsville coke.

RETORT OVENS LESSEN THE IMPURITIES IN COKE.

The theoretical yield, when applied to coke, signifies the coke obtained from 100 of coal by expelling the volatile matter and not permitting the combustion of any of the fixed carbon.

In beehive ovens, the yield of coke is from five to twenty per cent. less than the theoretical yield; in the Semet-Solvay retort ovens, we find in the large number of trials we have made on different coals, that the yield is greater than the theoretical by five to ten per cent., according to the coal under consideration. This is due to the fact that by the beehive method, much of the fixed carbon is burned, whereas, by the retort method, no fixed carbon is consumed because there is no admittance of air, and through the breaking-down of the gases much carbon is precipitated in and upon the coke.

The following figures illustrate by actual results obtained, the difference between coking in beehive and retort ovens. The importance of this increase of yield from a commercial as well as from a chemical standpoint is perfectly evident.

	Syracuse.	Dunbar.	Sharon.	Ensley.	Wheeling.	Total.
Kind of coal	Buffalo, Rochester and Pittsburg.	Connellsville.	Washington.	Alabama.	Connellsville.	
Weight of coal coked per day (tons)	112	224	112	540	270	1258
Per cent. yield of coke per day	72	73	72	73	73	
Weight of coke per day (tons)	80.6	163.5	80.6	394.2	197.2	916
Per cent. yield of coke in beehive oven from same coal	65	66	65	60	66	
Weight of coke from beehive oven	72.8	147.8	72.8	324	178.2	795.6
Per cent. increase in the yield of retort oven over beehive oven	10.7	10.6	10.7	21.6	10.6	

Further trials on well-known coals give the following results:

	Beehive. Per cent.	Retort oven. Per cent.	Gain. Per cent.
Pocahontas	62	83	33
Morris Run.....	60	80	33

It will thus be seen that the retort ovens actually lessen the percentage of sulphur, phosphorus, and ash impurities of the coke, by increasing the fixed carbon.

The sulphur in coal is present in three forms, as pyrites (FeS_2), or it is combined with carbon as a hydrocarbon, or it is present as calcium sulphate.

In the retort coke oven the organic sulphide is expelled and one-half of the sulphur of the pyrites, while the calcium sulphate remains unchanged. The sulphur remaining in the coke is almost invariably lower in percentage than in the coal.

The following are tests of sulphur in various coals coked in the ovens at Syracuse, and the sulphur in the coke made from these coals, also the volatile matter in the coals.

PER CENT.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Sulphur in coal....	1.95	0.73	1.62	0.67	1.25	0.99	2.8	3.8	1.7
Sulphur in coke....	1.75	0.68	1.44	0.66	0.94	0.90	2.7	2.7	1.5
Vol. matter in coal.	38.2	23.7	27.3	25.4	31.8	37.8	40.1	40.4	29.6
Sulphur in coke supposing none evolved in coking	3.155	0.956	2.228	0.898	1.832	1.594	4.675	6.377	2.414
Per cent. sulphur removed.....	44.32	28.95	35.36	26.53	48.67	43.54	42.25	57.66	37.85

VOLATILE MATTER IN RETORT COKE.

The volatile matter in retort coke is quite as low and sometimes lower than in beehive coke. In passing it may be stated that the customary method of determining the volatile matter in coke, as described by Blair, gives results which are slightly too high, due to combustion of some of the fixed carbon. To completely prevent oxidation of the carbon on heating over a blast-lamp for three and one-half minutes, a stream of hydrogen or nitrogen is gently passed over the coke in the crucible, thus keeping the coke in an atmosphere of an inert gas during the heating; by this method a coke will show a volatile of 1.25 per cent., whereas, by the customary method, 2.25 per cent. volatile would have been shown.

Fig. 4 is a sketch of the apparatus used for determining the volatile matter in coke. It consists of a small platinum crucible with a cover tightly fitting the top of the crucible on the inside; through the cover is an inlet tube passing well down into the crucible, and an outlet tube on the cover. About ten grams of

fine coke are placed in the crucible, the cover put on, and a gentle stream of hydrogen or nitrogen, about two bubbles a second,

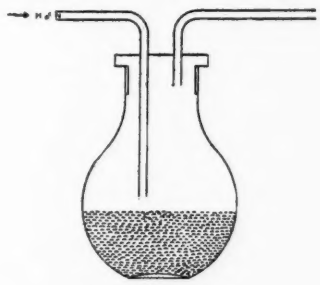

Fig. 4.

as indicated by a small bottle of water through which the gas passes, replaces the air and fills the crucible with the inert gas. The blast-lamp is then placed under the crucible and the coke heated for three and one-half minutes.

BY-PRODUCTS.

The by-products obtained from the distillation of coal in retort coke ovens are tar, ammonia, and gas, and from the gas may be recovered benzene and cyanides; all the by-products vary in quality and quantity with the composition of the coal, and are also affected more or less by the temperature to which the oven is heated. Generally speaking the quantity of tar and ammonia obtained is in direct proportion to the percentage of volatile matter in the coal. One containing seventeen per cent. volatile matter will yield $13\frac{1}{2}$ lbs. of ammonia, figured as sulphate, and 30 lbs. of tar, whereas one containing thirty-seven per cent. volatile matter will yield 27 lbs. of ammonium sulphate, and 110 lbs. of tar. We are not referring now to the western coals, known as dry coals, which are devoid of bitumen and coke with great difficulty and yield a small amount of by-products, but to the coals found in the bituminous, or semibituminous fields of Pennsylvania, Virginia, West Virginia, Tennessee, Alabama, or Nova Scotia.

From the large number of ultimate analyses which we have made of coals experimented upon in ovens, we find that coals having the highest percentage of hydrogen over and above that necessary to combine with the oxygen in the coal, are the ones which make the best coke, and produce the greatest quantity of by-products; in other words, a coal containing a high percentage of oxygen will not produce good coke, nor will it produce much tar and ammonia. If the analysis shows water of consti-

tution five to ten per cent. indicating the character of a lignite, the yield of by-products will be small and the coke of poor quality ; or having at hand the proximate analysis of a coal found in any of the above-mentioned localities, one may judge very closely the yield of by-products per 2000 lbs. of coal by referring to the following chart. A line is also given showing the yield of coke to

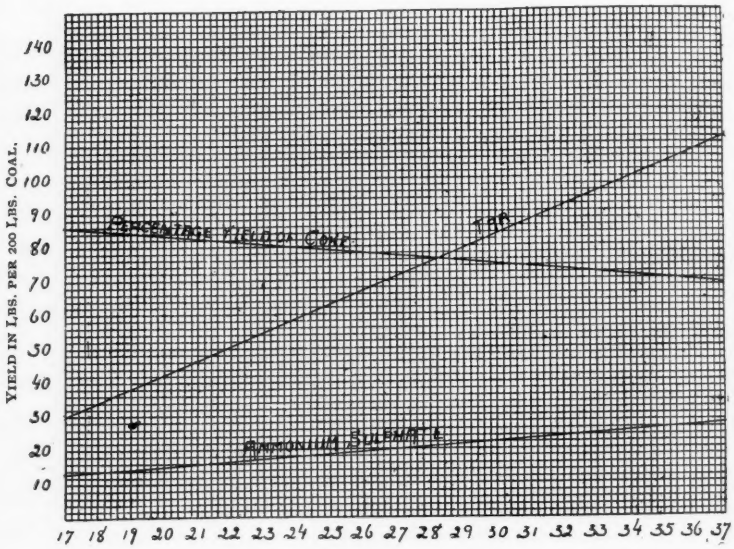

Fig. 5.—Chart showing lbs. of tar, ammonium sulphate per 2000 lbs. coal and percentage yield of coke for coals varying from seventeen per cent. to thirty-seven per cent. volatile matter.

be obtained. The higher the volatile matter the greater will be the increase in yield of coke over and above the theoretical. On this chart the increase in yield over the theoretical for a coal containing seventeen per cent. volatile is four per cent.; for one containing thirty-seven per cent. it is eight per cent.

AMMONIA.

Weak liquor is converted to crude gas liquor, aqua ammonia, and sulphate.

While ammonia is formed from the organic nitrogen of the coal and while it is true that those coals highest in nitrogen also produce the most ammonia, still the amount of hydrogen present

in the coal over and above that necessary to combine with the oxygen of the coal, has an important influence in the yield of ammonia.

Coking coals do not vary greatly in nitrogen, from 1.30 to 1.60 per cent., whereas the yield of ammonia from coals containing these two percentages of nitrogen is 13½ and 27 lbs. ammonium sulphate respectively. It will thus be seen that the yield of ammonia is not exactly in proportion to the content of nitrogen in the coal. It will also be noted that this yield is a comparatively small percentage of the theoretical yield of ammomonia from the nitrogen contained.

A coal of 1.30 per cent. nitrogen has a theoretical yield of 122.5 lbs. ammonium sulphate.

A coal of 1.60 per cent. nitrogen has a theoretical yield of 150.8 lbs. ammonium sulphate.

Thus in the first case eleven per cent. of the nitrogen is recovered as ammonia, and in the second case eighteen per cent. is obtained as ammonia.

William Foster[1] accounts for the nitrogen in coal when distilled in a gas retort as follows :

	Per cent.
Nitrogen of coal evolved as ammonia (NH_3)	14.50
" " " " " cyanogen	1.56
" present in gas as elementary nitrogen	35.26
" remaining in the coke	48.68

The addition of two per cent. of lime will increase the yield of ammonia ten per cent. This, however, could be done only with coals very low in ash.

The amount of nitrogen left in the coke varies greatly for the different coals. Many coals having very low nitrogen show the highest percentages of nitrogen in the coke. The following figures for nitrogen in coals and coke from them illustrates this point :

	I. Per cent.	II. Per cent.	IV. Per cent.	V. Per cent.
Nitrogen in coal	1.52	1.60	1.39	1.30
Nitrogen in coke	0.553	0.354	0.749	0.53
Volatile matter in coal	36.46	31.88	23.72	21.99
Nitrogen in coke if none evolved in coking	2.392	2.349	1.822	1.663
Nitrogen evolved as NH_3, CN and elementary nitrogen	76.88	84.51	58.88	68.13
Nitrogen of the coal recovered as NH_3	19.26	13.88	15.02	11.43
Evolved nitrogen, recovered as NH_3	25.02	16.39	25.51	16.78
Ammonia, figured as sulphate, recovered per 2000 lbs. coal (pounds)	25.36	20.93	19.67	14.00

[1] *J. Chem. Soc.*, 43, 105-110.

To determine at what stage of the coking process the ammonia is expelled from an oven, a measured volume of gas was drawn through acid at different intervals and it was found that ammonia was evolved at the following rate. Eight samples of gas were tested during the twenty-four hours of coking.

RATE OF EVOLUTION OF AMMONIA PER 2000 LBS. COAL.

	Lbs.
At the end of 1 hour	16.2
4 hours	21.1
7 "	19.8
10 "	22.5
13 "	17.5
16 "	13.9
19 "	8.5
22 "	1.7

The ammonia is collected partly in the hydraulic main, partly in the condenser, and the last traces are removed from the gas in the scrubber. The liquor collected from these places is of course very weak and must be concentrated by distillation with lime to free the fixed ammonia. The weak liquors contain ammonia in the fixed and free state and include the carbonate, sulphate, sulphide, and chloride of ammonium. The weak liquors are of the following composition :

	Grams per liter.	
	Free ammonia.	Fixed ammonia.
Hydraulic main	1.18	7.14
Condenser	8.2	2.1
Scrubber	10.5	0.9

By distillation and condensation a crude ammonia liquor of seventeen per cent. to twenty per cent. ammonia is obtained. The sulphur and carbon dioxide combined with the ammonia in the weak liquor, reappear in the strong liquor. The composition of this liquor is:

Ammonia	17 to 20 per cent.
Carbon dioxide	75 to 80 grams per liter.
Hydrogen sulphide	30 to 35 " "

The quantity of ammonium sulphide, of course, depends upon the amount of the sulphur in the coal. There is always carbon dioxide in the gas from the oven in excess of the ammonia, hence a large amount of ammonium carbonate is necessarily formed. The principal other impurity in the crude concentrated liquor is ammonium cyanide, often present in such quantities as to make it profitable to recover it as potassium ferrocyanide; the greater part of the cyanogen, however, passes away in the gas, and after passing the scrubber may be treated for its removal.

Instead of making the crude yellow gas liquor of commerce, as above described, the process of distillation may be so carried on as to remove the carbon dioxide and hydrogen sulphide, and a product formed which is perfectly colorless, containing twenty-nine per cent. ammonia, and known in the trade as aqua ammonia. The following table shows the relation of °Bé to per cent. ammonia in aqua ammonia :

AQUA AMMONIA.

Table adopted by National Ammonia Co.		Table by G. Gerhardt.	
Specific Gravity, 60° Fah.	Degrees Baumé (Gerhardt).	Per cent. ammonia.	Factor.
1.0000	10	0.0	0.0000
0.9930	11	1.6	0.055168
0.9864	12	3.3	0.1138
0.9793	13	5.05	0.1741
0.9726	14	6.80	0.23445
0.9660	15	8.33	0.2872
0.9594	16	10.17	0.35066
0.9530	17	11.88	0.4096
0.9467	18	13.88	0.47858
0.9400	19	15.63	0.5389
0.9342	20	16.42	0.6006
0.9281	21	19.25	0.6637
0.9221	22	21.12	0.7282
0.9191	22.5	22.07	0.76097
0.9161	23	23.03	0.7941
0.9132	23.5	24.00	0.8175
0.9102	24	25.00	0.8620
0.9073	24.5	25.98	0.8958
0.9045	25	26.98	0.9303
0.9016	25.5	27.60	0.9516
0.8986	26	29.00	1.0000
0.8959	26.5	29.69	1.0237

To meet the demands of manufacturers of fertilizers, the gases from the distiller may be absorbed in 60° sulphuric acid contained in a lead-lined tank called a saturator, and crystals of ammonium sulphate obtained. The color of the crude commercial ammonium sulphate is usually gray, but is sometimes blue. Blue sulphate brings a much lower price than the gray. The blue color is due to the presence of Prussian blue formed from the ammonium cyanide in the weak liquor. By special treatment of this liquor before distillation a gray sulphate may invariably be obtained.

TAR.

As previously stated the amount of tar recovered varies from 30 to 110 lbs. per 2,000 lbs. coal, according to the composition of coal. The tar, like the ammonia, is separated from the gas in the hydraulic main, condenser, and scrubber.

The quality of tar from retort coke ovens varies greatly; the

quantity as before stated depends upon the composition of the coal, the temperature of the ovens, and the pressure of the gas between the oven and the hydraulic main; the same may be said to be true of the quality of the tar. It is also true that coals, identical as far as the proximate analysis is concerned, sometimes produce tars which are widely different in composition. It is difficult to say why this should be so; it is probably due to slightly different conditions of operation, and partly due to a difference in the coal which is not shown in the proximate analysis. The relation of the carbon to the hydrogen in the volatile matter is different. A coal in which the hydrogen is a large percentage of the carbon in the volatile matter, produces a tar containing much naphthalene; and we find on the other hand that the amount of naphthalene in a tar from a coal very low in hydrogen is very small. To illustrate: In one of our plants the tar obtained is so highly charged with naphthalene that on distillation the very first distillate up to 100° C. solidifies, whereas, in another plant, the tar obtained shows only traces of naphthalene, though the coals used are almost identical, judging from the proximate analysis. Analyses of these two coals and the tar obtained are:

ANALYSES OF COALS.

	A. Per cent.	B. Per cent.
Volatile matter	34.20	32.68
Fixed carbon	57.15	59.40
Ash	8.65	7.92
Sulphur	0.93	1.19

ANALYSES OF TAR.

	A.	B.	I.	II.
Specific gravity	1.163	1.203	1.205	1.231
	Per cent.	Per cent.	Per cent.	Per cent.
Water	2.40	2.70	1.40	1.10
Light oil	4.60	2.03	3.12	1.63
Creosoting oil	1.26	0.50	0.29	0.34
Dead oil	22.81	16.40	25.09	19.23
Naphthalene	6.0	trace	0.20	1.72
Anthracene	0.6	"	0.19	0.24
Soft pitch	68.80	70.50	67.40	74.14

Tars A and B show what differences may exist in tars made from coals very similar in proximate analysis. I and II represent two tars from gas houses, which also vary greatly, but as a usual thing are found to be of a much higher specific gravity and to contain less light oils, making them inferior for the manufacture of benzene, and the dipping of paper for tarred paper.

The analyses of tar given above were made by a method which gives results that enable a tar distiller to judge of what the com-

mercial value of the tar is. A tar distiller wants to know how much light oil, naphthalene, dead oil, and soft pitch a tar will give. There is as yet no market for anthracene in this country. Most analyses given in books show too low a percentage of pitch. There is practically no market for hard pitch. To produce a salable pitch distillation must be stopped at 355° to 360° C. The method of analysis used for the determination of the commercial value of tar is as follows:

In the first place no test should be made on a quantity less than a gallon.

Method.—Weigh out ten lbs. tar in a measured cylinder, and in this way determine the specific gravity of the tar.

The thermometer in the distillation of tar should be placed one-half inch above the surface of the liquid.

Keep the tar at a temperature of 50° C. for twelve hours. Water comes to the surface, which is to be removed and measured, and is to be reckoned in the analysis of the tar.

Put the balance of the tar into a copper still, of two gallons capacity, and begin the distillation very slowly at first, the distillate coming one drop per second. Have a beaker of water, into which place a drop of the distillate when the light oil is coming over, to indicate the point when the light oil changes into heavy oil and sinks in water. The distillate is then turned into another receiver, and the light oil and water in the first receiver carefully measured. The distillation is then continued up to about 360° C., or to such a point as produces a roofing pitch in the still, which may be determined by taking a sample from the still, putting in water, and testing the cooled sample.

If it has cohesive properties, that is, if it makes a gum, it is of good quality. If it is brittle, the distillation has been carried too far, and the residue in the still will be hard pitch, which is unsalable.

The temperature of the condenser should be kept at 75° C. during this distillation. The distillate should stand for some twelve hours at a temperature of about 60° F. The roofing pitch in the still, after cooling, should be removed by unsealing the top, which is bolted, and turning the still upside down; upon gently heating the bottom of the still the pitch will drop out in one large cake. This is then weighed and constitutes the percentage of roofing pitch in the tar.

The distillate contains the creosote oil, dead oil, naphthalene, and a portion of the anthracene, it being necessary to have held in the pitch some of the anthracene to produce a pitch of the right quality for roofing purposes. The distillate with its crystallized naphthalene and anthracene is transferred to a Canton flannel cloth and compressed to remove the liquor as much as

possible by hand; then it is placed between one-quarter inch iron plates and put into a vise and pressed for about one-half day, every little while tightening the vise; this pressed cake represents the crude naphthalene and crude anthracene over and above the amount remaining dissolved in the dead oil. The liquor resulting upon compressing and removing the naphthalene and anthracene contains the creosoting and dead oil. This oil is placed in a small copper still of about one liter capacity. The distillate resulting up to 200° C. is the creosoting oil; the balance in the still is dead oil.

To separate the anthracene from the naphthalene melt up the material from which the oil has been pressed, put in a still and distil up to 280° C. (This distillate is crude naphthalene.) Now save the fraction distilling from 280° C. to dryness (this is anthracene mixed with a little anthracene oil.) Press this as with the larger amount before, and the solid matter remaining in the cloth is the crude anthracene. This subtracted from the total will give the crude naphthalene also.

PRACTICAL TEST FOR ROOFING PITCH.

The practical test for roofing pitch is to take a sample, place it in the mouth and chew it, and if there is a sufficient amount of cohesion to produce a gum, the roofing pitch is of good quality. This is a very crude test, but is the one used in the tar distillation works.

GAS.

A portion for heating ovens; the surplus for illumination, fuel purposes, or for power in gas engines.

The total volume of gas evolved from a coal is of course directly proportionate to its percentage of volatile matter and the heat to which it is exposed. This holds true of the gas from a retort coke oven, provided leaky flues do not admit air to burn the gas in the oven, or under conditions of excessive pressure gas is not driven into the flues and there burned. But in well-constructed and well-regulated ovens this need never occur.

The total volume of gas from a coal containing thirty-three to thirty-four per cent. volatile matter is about 10,400 cubic feet per long ton, or 9,280 cubic feet per 2000 lbs.; from a coal of twenty per cent. volatile matter, about 7000 cubic feet per long ton, or 6250 cubic feet per 2000 pounds.

The quantity of gas necessary to be returned to the oven for heating is from fifty to fifty-five per cent. if the coal is thirty-two to thirty-four per cent. volatile. Less gas is required to coke coals of low volatile composition. Thus Pocahontas coal containing nineteen per cent. volatile matter requires only two-thirds as much gas for coking as Connellsville coal, which contains thirty-two per cent. volatile.

I give below the results obtained from the coking of a coal in an isolated oven; analyses of this gas taken after passing the purifying box were made hourly during the period of coking, which was twenty-four hours.

Photometric readings were made every five minutes, the tests averaged and recorded for every hour calculated for a consumption of five feet per hour at 60° F. and thirty inches mercury, each candle-power being equal to 120 grams spermaceti per hour. The photometer used was a sixty-inch bar photometer.

The analysis of the coal used in this test was as follows:

	Per cent.
Volatile	35.71
Fixed carbon	59.36
Ash	4.93
Sulphur	2.4
Nitrogen	1.52

	Cubic feet.
Total volume of gas from 9,400 lbs. coal	43,747
" " " " " 2,000 " "	9,280
" " " " " 2,240 " "	10,400

Using this same coal in the entire twenty-five ovens for forty-eight hours and turning the excess or surplus gas into holders, we found that this excess gas amounted to 44.5 per cent. of the total gas; in other words:

Total gas	9,280 cubic feet per 2000 lbs. coal.
Percentage gas for coking	55.5 per cent.
Volume gas for coking	5,150 cu. ft.
Percentage of surplus gas	45.5 per cent.
Volume of surplus gas	4,130 cu. ft.

These figures represent accurately the distribution of the gas when making blast-furnace coke. If only domestic coke is to be the product, fifteen to twenty per cent. less gas will be required for the coking process.

The following are the records of gas analyses made hourly, and from a perusal of them we see that the methane at the beginning is very high, forty-six per cent., and that it soon falls to forty per cent. and remains at this figure for about twelve hours, and then begins to fall off until, at the discharge, the gas contains only 10.2 per cent. The hydrogen on the other hand starts in at 28.9 and is ever increasing, until at the end it has reached 77.0 per cent. The illuminants (olefines) are highest, 6.8 per cent., in the beginning and gradually diminish, until after sixteen hours they are practically nil. The carbon monoxide, nine per cent. in the first test, gradually decreases until in the last test four per cent. is found.

The high nitrogen in the early tests is due to an excessive suction on the oven:

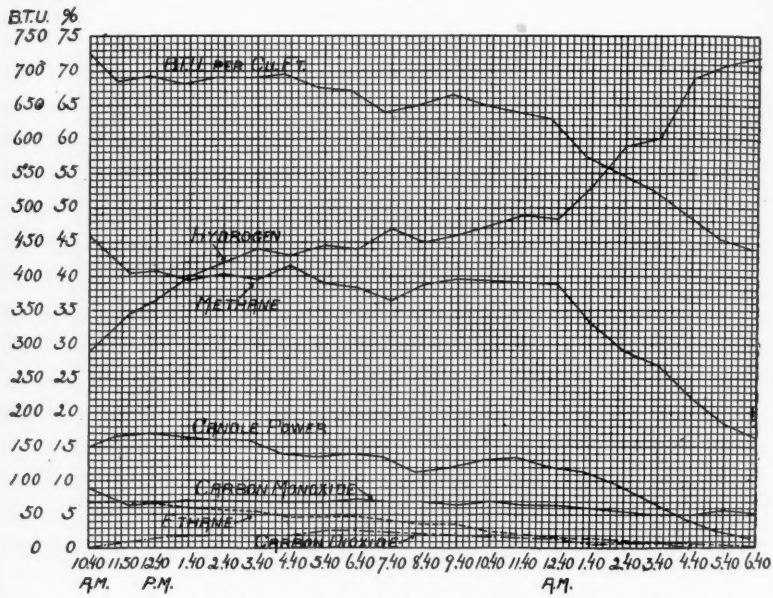

Fig. 6.—Hourly record of analyses, candle power and B. T. U. per cu. ft. of gas from one coke oven.

Time.	Carbon dioxide.	Ethylene.	Oxygen.	Carbon monoxide.	Methane.	Hydrogen.	Nitrogen.
10.40 A.M.	0.0	6.8	1.0	9.0	46.0	28.9	8.3
11.50	1.2	6.8	1.0	6.4	40.5	34.3	9.8
12.40 P.M.	1.6	6.7	0.7	6.7	40.8	36.7	6.8
1.40	2.0	6.0	0.6	6.9	39.5	40.2	4.8
2.40	2.0	5.6	0.4	6.8	40.3	42.1	2.8
3.40	2.0	5.5	0.3	6.8	39.6	44.0	1.8
4.40	2.0	4.8	0.4	7.0	41.5	43.3	1.0
5.40	2.5	4.7	0.5	7.0	39.2	44.7	1.4
6.40	2.5	4.8	0.8	7.2	38.8	43.9	2.0
7.40	2.3	4.2	0.5	6.9	36.4	47.2	2.5
8.40	2.3	3.6	0.4	6.8	38.9	45.2	2.8
9.40	2.1	3.7	0.3	6.6	39.7	46.0	1.6
10.40	2.1	2.7	0.3	7.0	39.3	47.5	1.1
11.40	1.5	2.2	0.4	6.6	39.2	48.9	1.2
12.40 A.M.	1.4	1.7	0.8	6.5	38.8	48.5	2.3
1.40	0.7	1.4	0.4	5.9	33.1	52 9	5.6
2.40	0.8	1.0	0.3	5.4	28.9	59.2	4.4
3.40	0.5	0.8	0.2	5.0	26.9	60.2	6.4
4.40	0.0	0.0	0.3	4.9	22.3	68.9	3.4
5.40	0.2	0.0	0.3	5.5	18.3	70.8	4.9
6.40	0.0	0.0	0.4	5.3	16.4	72.1	5.8
7.40	0.2	0.0	0.2	4.3	12.9	73.5	8.9
8.40	0.0	0.0	0.4	4.0	10.8	75.0	9.8
9.40	0.0	0.0	0.2	4.0	10.2	77.0	8.8

The following table shows the calorific value of the gas from hour to hour and also the candle-power:

Time.	Average candle-power for each hour.	Calories per cubic meter.	Calories per cubic foot.	B. T. U. per cubic foot.
10–11 A.M.	15.1	6539	185	734
11–12	16.7	6104	173	686
12–1 P.M.	17.2	6201	175	694
1–2	16.5	6088	172	682
2–3	15.8	6158	174	690
3–4	16.0	6135	174	690
4–5	13.9	6195	175	694
5–6	13.3	6004	170	674
6–7	13.9	5963	169	670
7–8	13.4	5739	162	642
8–9	11.3	5821	164	650
9–10	11.9	5931	168	666
10–11	12.9	5802	164	650
11–12	13.5	5748	162	642
12–1 A.M.	12.2	5621	159	631
1–2	11.4	5151	145	575
2–3	9.3	4871	138	547
3–4	6.8	4669	132	523
4–5	4.2	4377	124	492
5–6	2.6	4074	115	456
6–7	1.6	3927	111	440
7–8	0.0	3607	102	404
8–9	0.0	3439	97	384
9–10	0.0	3235	91	361

From a study of these figures it will be seen that as an illuminating gas it is not of much value after ten hours. In calorific value, however, it has diminished only slightly.

From the following table it will be seen that the volume of gas expelled per hour remains pretty nearly constant for seventeen hours and then falls off rapidly:

1. Time.
2. Cubic feet of gas expelled from the oven per hour.
3. Average of the several readings of the candle-power during each hour.
4. Total cubic feet of gas expelled from hour to hour.
5. The percentage of total cubic feet of gas expelled at the end of each hour.
6. Average candle-power of the total gas.

1.	2.	3.	4.	5.	6.
10-11	2032	15.1	....	..	...
11–12	2272	16.7	4304	9.8	15.9
12–1	2075	17.2	6379	14.5	16.3
1–2	1934	16.5	8313	19.0	16.4
2–3	1974	15.8	10287	23.5	16.2
3–4	2068	16.0	12355	28.2	16.2
4–5	1880	13.9	14235	32.5	15.9
5–6	1880	13.3	16115	36.8	15.6
6–7	1880	13.9	17995	41.1	15.4

1.	2.	3.	4.	5.	6
7–8	1974	13.4	19969	45.6	15.2
8–9	2068	11.3	22037	50.3	14.8
9–10	2162	11.9	14199	55.3	14.6
10–11	2256	12.9	26455	69.47	14.4
11–12	2162	13.5	28617	65.41	14.4
12–1	2068	12.2	30685	70.14	14.2
1–2	2350	11.4	33035	75.51	14.0
2–3	2162	9.3	35197	80.45	13.8
3–4	2350	6.8	37547	85.82	13.4
4–5	1598	4.2	39145	89.48	12.9
5–6	1410	2.6	40555	92.70	12.4
6–7	1034	1.6	41589	95.06	11.9
7–8	940	0.0	42529	97.21	11.3
8–9	889	0.0	43418	99.24	10.8
9–10	329	0.0	43747	100.00	10.4

In the above tables we have the means of determining the most advantageous disposition to make of the gas from a plant of retort coke ovens.

First, the first forty-five per cent. of the gas expelled may be received in a holder and used without enrichment, as is done with the gas from the ten Semet-Solvay ovens at Halifax. These ovens were erected to take the place of others of a different type which were a failure. Or, second, the entire gas from the ovens may be enriched and brought from 10.4 to 16 or 17 candle-power and used for illuminating purposes; or third, the entire gas may be pumped to street mains for domestic fuel supply, without enrichment.

In either of the two last cases producer gas would be substituted for the coke oven gas for heating the ovens. This is perfectly practical, and profitable, if there is a demand for all the coke oven gas.

The following table shows the composition of the surplus gas, and of the balance of the gas which would ordinarily be used for heating the ovens; Fig. 5 also represents graphically the analyses of gas, etc.

ANALYSES.

	Carbon dioxide.	Illuminants.	Oxygen.	Carbon monoxide.	Hydrogen.	Methane.	Nitrogen.
Surplus gas	1.8	5.5	0.6	6.4	40.5	40.2	4.9
Heating gas	0.8	1.2	0.3	5.6	60.4	26.8	4.9
Average	1.3	3.4	0.45	6.0	50.45	33.5	4.9

HEAT UNITS.

	Volume in per cent.	Volume per 2000 lbs. Cu. ft.	Volume per long ton. Cu. ft.	Calorific power. B. T. U.	Calorific power. Calories per cubic-meter.	Candle-power.
Surplus gas	45.5	4130	4732	685	6112	15.2
Heating gas	55.5	5150	5668	532	4734	8.3
Average and total..	100.0	9280	10400	608.5	5423	11.7

To compare with retort coke oven gas in composition and fuel value are taken figures of retort gas, given by C. D. Jenkins, State gas inspector of Massachusetts, in his report of 1896. For analyses of natural gas, average of figures given by Prof. F. C. Phillips, *Am. Phil. Soc.*, 17, have been adopted.

	Natural gas. Per cent.	Illuminating gas. Per cent.	Coke Oven gas. Per cent.	Water gas. Per cent.	Producer gas. Per cent.
Carbon dioxide	0.48	1.75	1.3	0.14	4.5
Illuminants	0.0	4.88	3.4	...	0.0
Oxygen	0.0	...	0.45	0.13	0.6
Carbon monoxide	0.0	6.82	6.0	37.97	25.5
Methane	92.47	33.90	33.5	7.65	1.0
Hydrogen	0.0	46.15	50.45	49.32	12.0
Nitrogen	7.05	6.50	4.9	4.79	56.4
B. T. U. per cu. ft.	984	623	608.5	381	138

From the above figures it will be seen that coke oven gas is greatly superior for heating purposes to producer and water gas, and only slightly inferior to illuminating gas. Of course, natural gas, composed so largely of methane, yields a much greater number of calories.

BENZENE OBTAINED FROM THE TAR AND FROM THE GAS.

Benzene and the other products of this series are evolved during the early stages of the coking process. They are condensed and appear in the lighter portions of the tar, or become fixed in the gas, and may be removed only by pressure and low temperature, or by dissolving in oils. By far the greater proportion of the benzene from a ton of coal is recovered from the gas, only about ten per cent. from tar. As the illuminating quality of a coke oven gas is largely due to the benzene (C_6H_6) contained, it is evident that the removal may greatly deteriorate its value for lighting purposes, while the heating value of the gas is only slightly affected. The first product obtained after treating the absorbent containing the benzene is known in the trade as "light oil." The light oil obtained from the gas is six and six-tenths lbs. to eight and five-tenths lbs. per long ton of coal, and varies with the percentage of volatile matter in the coal.

The light oil contains from fifty-eight to sixty-three per cent. of benzene, divided thus:

	Per cent.
Ninety per cent. benzene	57
Fifty per cent. benzene	2
Solvent naphtha	4

Distillation of this light oil gives a product distilling as follows:

Density at 15° C	0.92
First drop	81.5° C
At 100° C	50.0 per cent. distilled
At 125° C	66.0 " " "
At 150° C	71.0 " " "
At 170° C	74.0 " " "

From the distillation of this product the ninety per cent. and fifty per cent. benzene and solvent naphtha of commerce are obtained. The analyses of these products are as follows:

NINETY PER CENT. BENZENE.

Density	0.89
First drop at	81.5° C.
	Per cent.
At 85° C	40
At 90° C	77
At 95° C	86
At 100° C	91-92

FIFTY PER CENT. BENZENE.

Density	0.884
First drop at	87° C.
	Per cent.
At 90° C	7.5
At 100° C	52
At 120° C	90-91.5

SOLVENT NAPHTHA.

Density	0.88
First drop at	116° C.
	Per cent.
At 120° C	6
At 160° C	99-91.5

CYANIDES.

As in the case with ammonia, cyanogen is evolved in greatest quantity about the eighth to the tenth hour of coking.

The formation of cyanogen in illuminating gas has been accounted for by Kuhlman through the action of ammonia on carbon, carbon monoxide, and carbon disulphide in the following reactions:

$$C + NH_3 = CNH + H_2, \text{ or}$$
$$C + 2NH_3 = CN, NH_4 + H_2;$$
$$CO + NH_3 = HCN + H_2O, \text{ or}$$
$$CO + 2NH_3 = CN, NH_4 + H_2O;$$
$$CS_2 + 2NH_3 = CNS, NH_4 + H_2S.$$

In the retort coke ovens we have similar conditions to the gas retort. It is, however, different in that the charge of coal is much greater, and the temperature is not so high; the quantity

of cyanogen obtained therefore is not so great from the retort coke oven, for high temperature is conducive to high yield. We find on testing the gas from the oven before entering the hydraulic main, that both thiocyanate and cyanides of ammonia are present; but that on testing the liquor from the hydraulic main, we do not find any ammonium cyanide or ammonium ferrocyanide. Even though the temperature of this liquor in the main is low, and one would expect the ammonium cyanide to remain in solution, we find that in the struggle for ascendency, carbonic acid and other acids expel the cyanogen, and it passes on with the gas.

In the examination of the ammonia liquor from the condenser, we find only a small amount of thiocyanate present, but a comparatively large amount of ammonium ferrocyanide. The only explanation to offer for this is that ferrous sulphide is formed by contact of the hydrogen sulphide with the very large expanse of metal in the condensers. This ferrous sulphide in an atmosphere of ammonia as an alkali forms with hydrocyanic acid, ammonium ferrocyanide. In the scrubber we find thiocyanate, but no ammonium cyanide or ferrocyanide.

Thiocyanate found in the different liquors is:

In hydraulic main	1.501	grams per liter ammonium thiocyanate.
Condenser	0.0912	
Washer	0.0058	

The gas leaving the scrubber contains the cyanogen in the form of hydrocyanic acid, and when hydrocyanic acid is recovered by the usual method, *i. e.*, passing the gas through an alkaline ferrous carbonate or sulphide absorbing solution, by which potassium ferrocyanide is formed, we find a considerable amount of sodium thiocyanate in the solution. In fact, our tests show that in this absorbing solution the cyanogen is divided as follows:

	Per cent.
Cyanogen as $K_4Fe(CN)_6.3H_2O$	92.61
" KCNS	7.39

The cyanogen recoverable from coke oven gas, figured as potassium ferrocyanide ($K_4Fe(CN)_6.3H_2O$) amounts from 1.25 to 1.50 lbs. per 2000 lbs. of coal.

The amount of cyanogen recovered in weak ammonia liquors, as ammonium thiocyanate and ferrocyanide, if added to the above yield, would increase the yield of potassium ferrocyanide one-tenth lb. per 2000 lbs. of coal.

J. D. PENNOCK.

NOTE.

The Occurrence of Vanadium, Chromium, and Titanium in Peats.[1]—Attention has been called by Dr. W. F. Hillebrand[2] to the comparatively wide-spread occurrence of vanadium in a large number of minerals and rocks. He states that "Hayes in 1875 reported its occurrence in a great variety of rocks and ores. Quoting from Thorpe's 'Dictionary of Chemistry,' 'it is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands.....' It is further reported to comprise as V_2O_5 0.02–0.07 per cent. of many French clays, 0.02–0.03 per cent. of some basalts, 0.24 per cent. of a coal of unknown origin, and 0.45 per cent. of one from Peru, amounting to 38.5 per cent. and 38.0 per cent. of the ash, and noted respectively by Mourlot and Torrico y Meca."

Roussel[3] states that a basalt with a content of 0.707–2.378 per cent. of titanium contained 0.006–0.023 per cent. of vanadium. Gladstone,[4] however, states that it does not occur in the volcanic dust of Vesuvius. Terrèil[5] found it in iron ores. Stolba[6] also mentions its occurrence.

From the above the presence of vanadium could with reason be suspected in peat. In the hands of the writer were samples of peats from Hyde Swamps, one mile south of Pungo Lake near the Northern Junction of Beaufort and Hyde Counties, N. C. The approximate analysis of these peats gave :

Sample	Water.	Volatile matter.	Fixed carbon.	Ash.
Peat I.....	73.67	16.16	9.72	0.45
Peat II.....	71.58	17.42	10.31	0.69
Peat III.....	76.01	14.19	9.32	0.48

The water was determined by taking a cube measuring about eight cm. each way (from 700 to 800 grams) and bringing to a constant weight by heating for a number of hours not higher

1 Read before the North Carolina Section at the midwinter meeting.
2 *Am. J. Sci.*, 6, 209 (*1898*).
3 *Ber. d. chem. Ges.*, 6, 1417 *b*.
4 *Ibid.*, 5, 815 *b*.
5 *Ibid.*, 10, 731 *a*.
6 *Chem. Centrbl.* (*1897*), 121.

than 105° C. An analysis, approximate, of this dried peat gave the following results:

Sample.	Volatile matter.	Fixed carbon.	Ash.
Peat I	61.38	36.90	1.72
Peat II	61.35	36.20	2.45
Peat III	59.13	38.85	2.02

It was convenient to examine the ash of a large number of peats from this and other localities to ascertain the presence of titanium. We have found no statements regarding the presence of this element in these ashes, although such a surmise was logical. Neither does chemical literature, as far as we have been able to examine, give any mention of the occurrence of chromium in peats. Appended are the results of seeking for these elements in the samples mentioned above.

Sample.	Titanic oxide.	Chromium sesquioxide.	Vanadium pentoxide.
			Percentages in ash.
Peat I	0.490	0.0283	0.00107
Peat II	0.340	0.0343	0.0026
Peat III	0.491	0.0355	0.0031

In determining titanium the ash was decomposed according to the method of W. A. Noyes,[1] namely, by fusion with sodium fluoride and potassium pyrosulphate. The melt was brought into solution with Dunnington's[2] necessary precaution in mind; *viz.*, having from five to ten per cent. of sulphuric acid present. Hydrogen dioxide was added according to Weller's[3] well-known method and the titanium determined colorimetrically. All hydrofluoric acid was driven off in the fusion and the hydrogen dioxide was free from that acid as well. Hillebrand[4] has shown the necessity for this.

Chromium[5] and vanadium[6] were estimated according to the latest method of Hillebrand.

CHAS. BASKERVILLE.

UNIVERSITY OF NORTH CAROLINA.

[1] *J. Anal. Appl. Chem.*, **5**, 39.
[2] This Journal, **13**, 210.
[3] *Ber. d. chem. Ges.*, **15**, 2592.
[4] This Journal, **17**, 718; *Chem. News.*, **72**, 158.
[5] This Journal, **20**, 454.
[6] *Ibid.*, **20**, 461; *Am. J. Sci.*, **6**, 209.

NEW BOOKS.

VICTOR V. RICHTER'S ORGANIC CHEMISTRY OR CHEMISTRY OF THE CARBON COMPOUNDS, edited by PROF. R. ANSCHÜTZ. Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the eighth German edition. VOL. I, CHEMISTRY OF THE ALIPHATIC SERIES. Philadelphia: P. Blakiston's Son & Co. 625 pp. Price, $3.00.

There are at present three pretty clearly defined classes of works on organic chemistry: (1) elementary text-books, which aim to give a systematic account of the general principles of the science and of the more important typical compounds and their relations to each other; (2) larger text-books, containing large quantities of material necessarily omitted from books of the first class, —material which the student will find very useful to have always at hand on his study-table or at his laboratory desk, but most of which no student can ever master in all of its detail; and (3) handbooks, aiming to give a complete record of the facts of the science now known. The book before us is one of the best of the works of the second class. The work of revision, which is imperatively necessary at frequent intervals in this subject, has been ably executed by Professor Anschütz. The translation by Professor Smith is clear and very satisfactory. It is impossible to avoid some errors in proof-reading, of course, but such errors appear to be very infrequent.

The discussion of the general principles of nomenclature, on p. 57, is too short to be satisfactory, and the attitude assumed toward the proposals of the Geneva Commission is disappointing. Also the promise that "the more important suggestions of the commission will receive full consideration under the various classes of bodies" is not fulfilled in such a manner that a beginner is likely to get a clear idea of the Geneva nomenclature from the book.

The brief, clear, historical treatment of many topics is a very excellent feature and adds greatly to the value of the book.

W. A. NOYES.

TRAITÉ D'ANALYSE CHIMIQUE QUANTITATIVE PAR ELECTROLYSE. PAR J. RIBAN, Professeur Chargé du d'Analyse Chimique, etc., L'Université de Paris. Paris: Masson et Cie, 1899. vi + 304 pp.

This volume consists of four parts. The first part considers

certain elementary physical subjects, indispensable to those carrying out determinations in the electrolytic way, such as the laws relating to the electric current, apparatus for its measurement and for its control, as well as descriptions of various forms of apparatus used in electrochemical analysis. The subject-matter is presented in a clear, complete, and interesting form.

The second part deals with the electrolytic determination of the individual metals and non-metals. The author first mentions arsenic, which cannot be fully deposited electrolytically, and then gives a very extended account of the various suggestions which have been made for the estimation of antimony. Perhaps the order of presentation is of little moment, but experience has led the reviewer to the opinion that it is better to commence with simple acid solutions, *e.g.*, copper in nitric acid, and gradually advance to those examples, which from natural conditions are more difficult to handle. This portion of the book is very complete in its presentation of the methods of all persons who have labored in this field. Here and there names of authors appear incorrectly spelled, and attached sometimes to methods which did not originate with them. This, however, is immaterial, for the student of the volume is given a very exhaustive description of what has been achieved, and is left to ascertain for himself which methods are the most satisfactory for his purposes.

The separation of the metals constitutes the third section. The first example is that of antimony from tin in a solution of sodium sulphide. This is far from being an easy problem. The method is beset with difficulties which even the most experienced have had trouble to remove.[1] The numerous methods given for other separations have in nearly all instances proved entirely satisfactory.

In the fourth part the author gives very excellent and explicit directions for the analysis, in the electrolytic way, of many alloys and commercial products. For this he deserves the thanks of all interested in the extension of the methods which have been successfully worked out for two or three metals when present in the same solution. On page 275 the student is directed in analyzing cinnabar, to dissolve it in hydrobromic acid, and after neutralizing with caustic potash and adding an excess of

[1] See *Ztschr. angew. Chem.* (*1897*), Heft 10; *Ztschr. Elektrochemie*, 4, 245.

potassium cyanide to proceed with the determination of the mercury. Time would be saved and disturbing constituents be eliminated by simply digesting the mineral with sodium sulphide, in which it is soluble, and after the removal of the insoluble parts by filtration, proceeding as directed under the determination of mercury. It is a great pity that literature references are omitted from the entire text.

Tables, showing the E. M. F. of various batteries, factors for the calculation of certain electrolytic data, electrochemical equivalents, the intensity of current expressed in volumes of electrolytic gas with their equivalents in amperes, resistances of metals and alloys, etc., etc., conclude the book, which is well printed and illustrated. It deserves a prominent place in electrolytic literature. EDGAR F. SMITH.

PHYSICAL CHEMISTRY FOR BEGINNERS. BY DR. CH. VAN DEVENTER. With an Introduction by PROF. J. H. VAN'T HOFF. Authorized American edition from the German edition, translated by BERTRAM B. BOLTWOOD. New York: John Wiley and Sons. 1899. x + 156 pp. Price, $1.50

THE ELEMENTS OF PHYSICAL CHEMISTRY. BY J. LIVINGSTON R. MORGAN, PH.D. New York: John Wiley and Sons. 1899. viii + 299 pp. Price, $2.00.

The reviewer has already[1] called attention to the need of a text-book on physical chemistry presenting the main facts and theories of this important branch of the science in a form not demanding too much preparation in physics or mathematics on the part of the student, and he is much pleased to note the appearance of these two books which go far towards filling this need. With such books at hand there is no reason why instruction in physical chemistry should not be given in even our smaller universities and colleges. A knowledge of the rôle that ions play in the reactions of analytical chemistry throws such a flood of light on that subject that it ought to be acquired by the student at the same time he is practising analysis in the laboratory. Instead of deferring the study of physical or theoretical chemistry until after courses in qualitative and quantitative analysis have been completed, it should be taken up along with them. The danger of work in analytical chemistry degenera-

[1] See the review of Clarence L. Speyers' "Text-Book of Physical Chemistry," in this Journal, 20, 389 (*1898*).

ting into mere routine and the acquisition of manipulative dexterity would certainly be avoided in a large measure by so doing.

These two books are in many respects complementary to each other. Boltwood's book is the more elementary, containing much that is usually given in good courses in beginning chemistry. In it but little space is devoted to methods, experimental or theoretical, and the treatment is strictly non-mathematical. The general plan is to state carefully laws and principles and then to illustrate them by remarks, historical, critical, etc.

Morgan assumes that the student has a knowledge of the rudiments of calculus, and to a not inconsiderable extent gives the mathematical derivation of many laws. He also sketches in broad outlines the chief pieces of apparatus and modes of using them, that have proved of such great service in the development of physical chemistry.

While Boltwood hardly more than touches upon the subjects of electrochemistry and ionization, Morgan treats of them excellently and at length, the doctrine of ions appearing all through his book. On the other hand, Boltwood takes up in some detail photochemistry and the periodic law, which are barely mentioned by Morgan.

Errors of importance are scarcely to be found in either book. As to the translation, although the translator in "closely following the German text in nearly all cases" (p. vi.) has in places let the German idiom appear too glaringly, yet on the whole he has succeeded in attaining a commendable smoothness and clearness of language. The reviewer would, however, deprecate the use of the expression "heat toning," inasmuch as heat effect expresses the same thing in good English.

The two books as issuing from the same publishing house are very similar in their make-up, the typography, presswork and binding being practically the same. C. E. LINEBARGER.

THE MICROSCOPY OF DRINKING WATER. BY GEORGE CHANDLER WHIPPLE. Biologist and Director of Mount Prospect Laboratory, Brooklyn, N. Y. First edition. New York: John Wiley & Sons. 292 pp.

It may without doubt be safely assumed that there are few water analysts who would not concede the value of a carefully conducted and intelligently interpreted microscopical examina-

tion of the suspended matter and sediment often found in drinking water, and it is quite conceivable that the result of such an examination may be a determining factor in deciding the question of the fitness, or the contrary, of a water for drinking purposes. And, whilst it must be admitted that, in the majority of cases, chemistry alone is competent to enable an expert to decide upon the quality of a water, the fact that there are many occasions in which an appeal to the microscope may be of great value and importance, is a good *raison d'être* for such a work as this.

Following a brief but interesting historical survey of the study of the micro-organisms in water from the time of Hooke and Lieuwenhock, is a chapter on the object of the microscopical examination of water, and this by an excellent one on "Methods of Examination," which, while more elaborate than the majority of chemists could find time to employ, must be regarded as an essential guide to the technical details necessary to complete work. Chapters on "Limnology," on "The Geographical Distribution of Organisms," on "Odors in Water Supplies," on "Storage of Water," on "The Growth of Organisms in Water Pipes," are followed by chapters on "The Classification and Description of Micro-organisms." A very useful bibliography and numerous unusually well-executed plates, wherein the experienced operator in this line of work will find many an old friend well portrayed and the beginner a very reliable guide, complete a work of much value to whom it may concern.

W. M. MEW.

THE SPIRIT OF ORGANIC CHEMISTRY. AN INTRODUCTION TO THE CURRENT LITERATURE OF THE SUBJECT. BY ARTHUR LACHMAN with an Introduction by PAUL C. FREER. The Macmillan Co. pp. xviii + 229. 12 mo. Price, $1.50.

The point of view of the book is made evident by a few sentences from the Introduction: "How can he [the student] ever hope to master the general classification, let alone the minor details, which must become a part of his very being, if he too wishes to do his share, however small, toward completing and rounding out the still unfinished structure? The answer is plain: "he can do this only by comprehending the *spirit of the science*, by learning its great theories, not as mere mnemonic efforts,

but as the result of a development for which many of the most earnest and acute minds known to the history of science have fought and toiled."

According to the preface the book is intended primarily as a supplement to text-books of organic chemistry. The author gives some with detail the views which have been held and now prevail on some of the leading questions in organic chemistry. These are the chapters: 1. The Constitution of Rosaniline; 2. Perkin's Reaction; 3. The Constitution of Benzene; 4. The Constitution of Acetoacetic Ether; 5. The Uric Acid Group; 6. The Constitution of the Sugars; 7. The Isomerism of Maleic and Fumaric Acids; 8. The Isomerism of the Oximes; 9. The Constitution of the Diazo Compounds. E. H.

DIE CHEMISCHE ENERGIE DER LEBEN DEN ZELLEN. By DR. OSCAR LOEW, U. S. Department of Agriculture, Washington, D. C. München, 1899.

This little volume of about 170 pages must be looked upon as a continuation of the investigations published by the author, treating of the difference between the living and dead forms of protoplasm.

The forerunners of the present publication are entitled respectfully, "Die chemische Ursache des Lebens," and "System der Gift wirkungen."

Though the titles would indicate entirely different subjects, they are yet the same in so far as Professor Loew has shown that poisons owe their power to their effect upon the living protoplasm, which is chemically a very active compound, but passes into a more stable product upon being deprived of life.

The book under discussion treats of the qualitative differences between living and dead protoplasm, and likewise the differences between various kinds of protoplasm. That these must exist is evident from many facts, as, for instance, that we possess some living organisms, which thrive at a temperature which is death to others. By physical differences as well as pathological and toxicological ones, the protoplasm of different organisms shows difference of behavior, which is exhibited by greater or less resistance to the action of chemicals. While the book contains mainly the author's own observations, it gives a place to those of others, with references to the literature, so that it can be looked

upon as a good exposition of the various views upon a subject, the development of which is due to the labors of the author himself. The observations are of so manifold a nature, that the perusal of the book cannot fail to be of value to all interested in the subject. H. ENDEMANN.

A HISTORY OF PHYSICS IN ITS ELEMENTARY BRANCHES, INCLUDING THE EVOLUTION OF PHYSICAL LABORATORIES. BY FLORIAN CAJORI. New York and London: The Macmillan Co. 1899. viii+322 pp. 12mo. Illustrated.

In this convenient volume the author sketches the progress of the growth of mechanics, light, electricity and magnetism, meteorology and sound under the Greeks, the Romans, the Arabs, in Europe during the Middle Ages, and the Renaissance as well as through the succeeding centuries to the present time. There are also chapters on the atomic theory, the causes of failure of Greek physical inquiry, gunpowder and the mariner's compass, and the inductive method of scientific inquiry. The author feels that "some attention to the history of a science helps to make it attractive," and has written the book in hopes of stimulating students and teachers of physics. Dr. Cajori cites a sentence written by Ostwald, who points out as a "defect in the present scientific education of youth, the absence of the historical sense and the want of knowledge of the great researches upon which the edifice of science rests," and he hopes that this volume will assist in remedying the defect.

The necessity of limiting the book to 300 pages has caused great condensation of statement, and prevented elaboration of principles; students who wish, however, to pursue further special lines, will find abundant references to literature throughout the volume; these show a wide acquaintance with the sources of information on the part of the author. Biographical sketches of those who have distinguished themselves by their notable discoveries and inventions are among the features of the volume.

In looking through this record one cannot but notice the occurrence of national jealousy in respect to priority of discovery. Germany, France, England, Holland, Italy, and at a later period the United States of America, each puts in a claim for having taken the first step in several prime discoveries and

inventions. The cases of the thermometer and of the electric telegraph will occur to every one. In many cases the conflict for priority is due to the fact that similar thoughts occur independently to more than one person, and oftentimes an invention is a growth to which several individuals have contributed. Few philosophical instruments are perfect at their birth, the barometer being a notable exception.

Professor Cajori's book can be recommended to students who really want to master the historical aspects of physical science.

H. CARRINGTON BOLTON.

CHEMISTRY AND METALLURGY APPLIED TO DENTISTRY. BY VERNON J. HALL, PH.D., Professor of Chemistry and Director of the Chemical Laboratories in the Dental School and in the Woman's Medical School of Northwestern University. xii + 246 pp. Evanston, Ill.: The Technical Press. 1898.

There are, probably, many members of the American Chemical Society who will have but a vague idea as to the precise field which this book is designed to fill. For the benefit of such members, it may be said that the book is but one recognition of a general change in methods of instruction now actively progressing in dental schools; namely, the introduction of really meritorious courses in the sciences of pathology, anatomy, physiology, and chemistry, as necessary adjuncts to the purely practical courses in operative dentistry and dental prosthesis.

The metal work of dentistry being of such eminent practical importance to the profession, it naturally follows that metallurgy is that department of chemical teaching which is most emphasized in dental schools. Hence a demand for specialized textbooks on "dental metallurgy."

We do not think that the book before us is destined to take any prominent place in the development outlined above; unless, perhaps, as an adjunct to Professor Hall's lectures. Its laying out of a systematic laboratory course on the physical properties of metals is timely and meritorious; as is also the practice in the refining of certain metals. The work is decidedly weak, however, in two points: it is replete with partial truths, which are almost unavoidably uninstructive or misleading; and it barely touches upon the philosophy of the subject-matter. It therefore fails as a compilation, or as an index to progress—both of which

results might be conserved in a book of equal size, provided ordinary quantitative physical and chemical data (which students cannot remember) were tabulated, and the space thus saved devoted to discussions of the rationale of essentials.

The quotation that follows has been selected at random, and fairly represents the general character of the statements. We find only this in explanation of cupels and cupellation: "cupels are small articles made of bone-ash and used in the process of cupellation. Bone-ash absorbs the oxides of almost all metals, particularly those of lead, hence it is used in purifying gold and silver, which do not oxidize." G. H. MEEKER.

A TREATISE ON PHOTOGRAPHIC OPTICS. By R. S. COLE, M.A., Late Scholar of Emmanuel College, Cambridge; Assistant Master, Marlborough College. Illustrated. New York: D. Van Nostrand Co. 1899. 330 pages. Price $2.50.

This is a modern book covering in a very satisfactory manner the important principles of optics as applied in photography. The matter is divided into seven chapters treating of the General Theory of Light; Elementary Theory of Lenses; Aberration; Correction of Aberration and the Design of Lenses; Lens Testing; Exposures, Stops, and Shutters; Enlargement, Reduction, Depth of Focus, and Halation. As far as is possible, consistent with thoroughness, the discussion is carried on with the aid of very elementary mathematics only, the formulas and equations introduced corresponding to about what is found in our usual college courses in physics.

The chemistry of photography is not touched upon at all but in other directions the book contains much practical information, especially useful to the investigator or to the manufacturer of photographic apparatus rather than to the every-day commercial photographer. The scientifically inclined amateur who desires to get the best results from the appliances at his command or who wishes to improve understandingly on what he has, will find in this book much of the needed help. For example, the chapter on exposures, stops, and shutters explains, in a very concise way, the principles which should guide in the construction of shutters, and their action and efficiency in very short exposures and gives results which the student might otherwise have to search through many volumes of journals and annuals to find.

What is given on enlargement and reduction takes up practical details more fully than is true of other parts of the book and appears to be well-written and useful. On the whole the work can be heartily recommended to the class for which it is written.

J. H. LONG.

ANLEITUNG ZUR DARSTELLUNG CHEMISCHER PRAPARATE. Ein Leitfaden für den praktischen Unterricht in der anorganischen Chemie. VON PROFESSOR DR. H. ERDMANN in Halle. Zweite Auflage, mit 15 Abbildungen im Text. Frankfurt a. M.: H. Bechhold. 1899. viii + 92 pp.

The first edition of this book has won for itself a wide-spread reputation as a text-book for the preparation of chemical compounds. Dr. Erdmann is an exception to the general rule of German chemists. He is a firm believer in the supremacy of inorganic chemistry, and the methods he has introduced in the study of this subject will be acknowledged by most teachers as a progressive step. The author carefully points out in his preface to this edition that previous to the appearance of his book very little time was devoted in laboratory instruction in the preparation of inorganic compounds. Although it has always been recognized that the study of organic chemistry is best carried out by the preparation of a number of typical compounds, yet the experimental study of inorganic chemistry has mostly been limited to test-tube reactions. Dr. Erdmann has been a very active factor in changing this point of view, and the chemists of the inorganic schools both here and in Germany are requiring a more and more thorough drill in chemical preparations. Such a method brings out the manipulative skill and causes the student to exercise his experimental ingenuity more than any other thing in the study of chemistry. If students were required to make their chemicals on a scale sufficiently large for practical use, the majority of them would be better chemists. And it is not in the preparation of fanciful chemicals that the best education is obtained, but in the making and purification of the common substances which are met with every day. Another point which the author insists upon is the use of raw materials in sufficient quantity to give the student a good idea of the comparative amounts of final products obtained in each case; and this is a point which should not be overlooked, for production is a very essential factor in such a course. A

student who cannot obtain more than a one or two per cent. yield in the preparation of chemically pure sodium chloride, for example, will never make his living as a chemist. The synthesis of inorganic compounds is just as important a subject in that field as the synthesis of compounds in the organic field, but strange to say there are few very satisfactory text-books on this subject. We are overcrowded with volumes relating to the analytical side of inorganic chemistry, and but few teachers seem to have considered the other. But sometimes it requires more chemical knowledge and skill to build up a compound than it does to analyze it. The author has chosen his synthetic examples with good taste, and in most cases he gives methods which are of a practical nature. Another point of convenience and instruction which makes this volume something more than a mere recipe book is that the description of every preparation is accompanied by a clear explanation of the chemical reactions entering into the process, together with simple tests by means of which the purity of the compound obtained may be ascertained. There is one feature, however, which might be somewhat improved upon, and that is, references to the literature of the subject. In this edition, these are very limited, and consist for the most part of references to the author's own text-book on inorganic chemistry. Of course the majority of the methods described in this book, especially with regard to the details of precautions and the manner of manipulation, are original; but, nevertheless, there are other methods and other ideas on the same subject which should not be ignored, and a larger enumeration of references to the latest chemical literature would render the book more valuable and useful.

But on the whole, Dr. Erdmann has given us a book full of valuable matter, and his practical suggestions scattered so lavishly throughout the description of each preparation will be welcomed with delight by both teacher and student, and the volume deserves its title of "guide" in every sense of the word.

J. MERRITT MATTHEWS.

ERRATUM.

In the July (1889) issue, page 624, in lines 10, 7, and 4 from bottom, for "s=" read "S=".